Chapter 13

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Planning and realisation of Soil remediation

A successful remediation plan has to be based on the information gained during the preliminary diagnostic works, which are done before taking the decision to start a remediation project. The following check list should be worked out and carefully studied before starting with the actual design of the technical work.

1) What are the types and chemical nature of the pollutants determined at the site?

a) Organics b) Inorganic substances

2) What are the Dimensions and scale of pollution?

a) Is the pollution localised?
b) Is it of the dispersed type?
c) How urgent is the remediation plan?

3) What is the risk level?

a) Low risk level
b) Medium level
c) High risk level

4) Which technical measures are thought to be most suitable for carrying out this project?

a) In place (*In situ*)?
b) Ex-situ? And if yes, should the soil be transported to a special facility? Should the remediation be carried out in a prepared bed system, or in tank?

5) Are there any financial restrictions on choosing the technical method of remediation?

6) Which method is technically suitable and financially fitting in the economic framework of the project?

Categories of pollutants:

In fact a pollutant can be any environmentally harmful substance that is accidentally or on purpose transported to the soil. Yet for the sake of planning, a common rather simplified classification that enables selection of the suitable remediation method may be sought. The following check list helps to limit the uncountable substances that may pollute the soil into few categories, having similar chemical and physical properties, and in most cases having comparable degrees of response to a given remediation process.

- Are the pollutants in the present case chemically characterised and identified? If yes, are they solids, NAPL's or leachates?
- Are they organics or non-organics? If organic, are they aliphatics or aromatics? If aromatics are they halogenated
- How high (low) are their molecular weights? (From the tables)
- Are they volatile or of low volatility?
- Are they (for organics) polar or non-polar? What is their degree of solubility (high, low)
- Is their any information about their biodegradability?
- If inorganic, of which category are they: metals, metal cations, waste - acids and alkalis? Are they easily oxidisable compounds? Are there any inorganic cyanides?

The careful workout of this check list as we will see later is a very important step on the right way to select the appropriate method of remediation. Other factors such as the scale of pollution and financial restrictions may impose revision of the decisions taken at this stage.

Scale of pollution

Results of sampling and chemical investigation supply enough information about the spatial dimensions of the pollution case, which is supposed to be treated. Pollution cases may according to their spatial dimensions be classified into the following two main types:

1.Localised pollution cases:

These are cases resulting from spill accidents, where materials spilled are known and the risk is at minimum when quick measures are taken. In these cases, remediation is mostly carried out in situ. Material safety data sheets supply information on the pollutant or the hazardous material forming the spill, so that immediate actions can be taken. One speaks also of localised pollution when the source of pollution is known such as leaking tanks, landfills or old industrial facilities. In such cases pollution would be spreading from the source in a flow pattern, which is more or less localised, and showing concentrations that decrease with increasing distance from the source of pollution. The flow pattern and rate of decrease of contaminant's concentration with increasing distance from the source can be characterised by careful sampling, investigation and mapping of the results.

2.Diffused pollution cases

Pollutants entering the soil will try to spread in both horizontal and vertical directions, whereby the dimensions of transport and diffusion will depend upon the saturation of the soil and upon its hydraulic and lithological character. When pollutants reach to the ground water its further transport will as it was said before depend upon the lithological character of the aquifer. Some aquifers due to this property may be selective in transporting material reaching the saturated zone. As an example one may consider the case of nitrates reaching the saturated zone in a fine-grained lime stone aquifer (micrite, chalk). In this environment, the nitrates can persist for very long times and can attain very high concentrations by accumulation. They are safe of being denitrified by dentrification bacteria, simply because the fine-grained chalk has very small pore sizes. These impede penetration of such microorganisms into the aquifer. The same phenomenon is also responsible for the accumulation of many substances in the ground water. Such contaminants, which have been seeping and accumulating in soil over long periods form immense scale of pollution that may be extending over huge spatial dimensions. Accumulation of same scales may also occur when materials that were bound by complex formation on humic substances are released due to change of the chemical environment, and then dispersed within the soil. Such cases of wide spatial dimensions, which are not localised or characterised by a source and flow patterns are normally described as diffuse cases of pollution. Their characterisation, mapping and remediation needs more detailed planning and technical installations than localised cases.

3.Risk level

Risk levels of contaminants should be determined according to the information collected on the chemical and physical properties of the potentially toxic material and its degree of dispersion in the area of investigation. Information on bioavailability and mobility of the material may indicate a low risk level if the toxic material is in an immobile form, or a non bio-available form with no impact on the environmental conditions. However, continuous monitoring is important in such cases, where no immediate risk exists, yet possible problems are expected on change of the chemical or physical conditions. In cases where immediate risk exists such as after spill accidents or the discovery of old toxic deposits resulting from old landfills, military or industrial sites measures for remediation should be started or carried out within short times.

4. Remediation technologies.

According to the scale of pollution, the risk level and the financial and time constraints on the remediation project, treatment of the soil may take place immediately in place *(in situ)* or the soil may be transported to special facilities where remediation may be carried out in special reactors or vessels, that are specially designed for this purpose *(in tank method)*. An example of this process is the washing of heavily polluted soils in special tanks. The polluted soil may also be transported and spread on a surface prepared to prevent the spread of contamination in lateral and vertical directions. Beds prepared in this way form the so-called prepared beds upon which the remediation process will take place. This method is especially suitable for soils contaminated by oil products. Generally speaking, however, four classes of remediation technologies are known. These are:

- Chemical and physical methods
- Biological methods
- Fixation methods (also storing and immobilisation)
- Thermal destruction methods.

Following diagram (Fig. 105) shows the main types of remediation technologies in a schematic way.

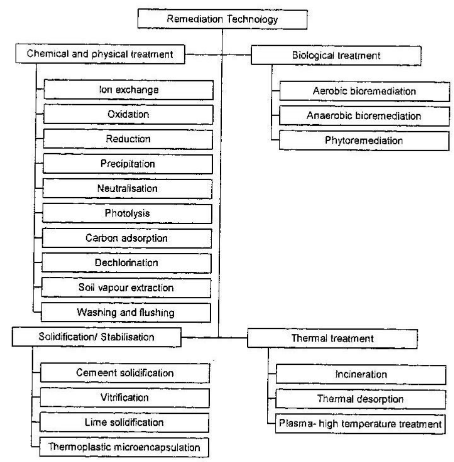

Fig. 105 Common remediation technologies

Some of the above mentioned methods may require specific technical installations (tanks and prepared beds), others may be suitable for use in place (in situ) still others may be suitable for all three operational modes of remediation. The following table(table 27) shows roughly the specific mode or modes suitable for each of the above-mentioned techniques.

Operational mode (s)	Suitable remediation technique
In situ	Soil vacuum extraction (SVE), Soil flushing.
In situ or in prepared beds	Carbon adsorption, Ion exchange.
In situ or in tank	Thermal stripping, dechlorination, Cement solidification, Vitrification, Lime solidification Thermoplastic microencapsulation.
All (In situ, in tank or in bed)	Neutralisation, Oxidation, Bioremediation (all methods).
In prepared bed	Photolysis.
In prepared bed or in tank	Precipitation, Reduction, Carbon adsorption, Ion exchange.
In Tank	Pyrolysis, Infrared, Rotary kiln, Fluidised bed, Soil washing.

Table 27 The different operational modes with their corresponding remediation techniques based on (BOULDING, 1995)

From the table one can clearly see that technologies like vacuum extraction and soil flushing are mainly done in situ, while bioremediation methods are all suitable for all operational modes. This factor plays a role in the financial planning of the remediation project that should be taken into account. The main decisive role, however, is played by the effectiveness of the method to the type of pollution encountered. In the following each of the above-mentioned technology will be shortly described.

1.Chemical and physical remedial techniques:

The aim of all chemical and physical methods of remediation is to change the chemical environment in a way that transport of toxic substances to other elements of the soil system is prevented. Exampl4es here can be given by transport to plants; to ground water; or to soil organisms). Such preventive measures may include decreasing mobility, change of chemical constitution or any of the factors, on which it has been elaborated in chapter 8. Chemical and physical methods of remediation include the following:

a) Oxidation

Oxidation is a common highly effective remediation technology for soils contaminated by toxic organic chemicals and cyanides. Oxidising agents used in this technology include a wide range of substances among which the most common are hydrogen peroxide, ozone and potassium permanganate. All three methods are according to EPA[4] of high treatment efficiency, reaching over 90% at short times in many cases. For example efficiency reaches. >90% for unsaturated aliphatic compounds such as trichlorethylene (TCE) as well as for aromatic compounds such as Benzene.

The reaction, if hydrogen peroxide is the oxidising agent used, takes place according to the following equation:

$$3H_2O_2 + C_2HCl_3\,(TCE) \rightarrow 2CO_2 + 2H_2O + 3HCl$$

Ozone destruction of toxic contaminants takes place in the following manner:

$$O_3 + H_2O + C_2HCl_3 \rightarrow 2CO_2 + 3HCl$$

Still using the same example i.e. oxidation of trichlorethylene, the reaction, if potassium permanganate ($KMnO_4$) was used, takes the following path:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl$$

Oxidation technology has been successfully used for in situ remedy at source areas as well as for flume treatment. It is mostly used for benzene, ethylbenzene, toluene and xylene (BTEX) as well as for PAH's, phenols and alkenes.

b) Ion exchange and precipitation

Soil components with high CEC values are capable of binding positively charged organic chemicals and metals in a way that makes them chemically immobile and thus reduce the risk imposed by them on the soil environment. Addition of soil conditioners such as synthetic resins zeolites or clays may help increasing the CEC characteristics of the soil and thus enhance the binding of positively charged contaminants on the negative functional groups of the soil matter.

[4] EPA 542-N-00-006, September 2000. Issue No. 37

c) Photolysis

Photolytic degradation technology depends upon degrading the organic contaminants with Ultraviolet radiation. This may be carried out using artificial UV light or just by exposing the soil to sunlight, which may be sufficient for degrading shallow soil contaminants. This process can be carried out in situ or in prepared bed. However, deeply contaminated soils must be excavated and transported to special facilities, where the process would be carried out in special tanks. A combination of Photolytic degradation and bioremediation may be achieved by adding micro-organisms and nutrients to the soil after the photolytic treatment.

d) Adsorption on granulated active carbon (GAC)

This technology depends upon the tendency of most organic compounds to adsorb on the surface of activated carbon. Adsorption tendency increases with the molecular weight boiling point of the organic material. Thus we find that the technology of adsorption on granular activated carbon (GAC) is best suitable for volatile organic compounds; hydrocarbons of high molecular weights; halogenated volatile organic compounds(VOC) and their halogenated forms; as well as some explosives and pesticides.

Remediation through adsorption on activated carbon is a method that can be carried out in the liquid phase as in treatment of ground water or in the gas phase as in treating off-gases from soil vapour extraction remediation methods. As a matter of fact one of the earliest applications of this method was the use of (GAC) in adsorbing military gases by gas masks in the first world war.. Adsorption on activated carbon is a process carried out ex-situ in special tanks or in prepared beds. It is principally used to treat toxic gases, solvents and organically based odours. However, impregnation of activated carbon with additional chemicals may be helpful in controlling some inorganic contaminants such as hydrogen sulphide, mercury or radon.

e) Reductive dechlorination

Reductive dechlorination is a quite effective technology with the help of which chlorine in polychlorinated organic compounds can be removed or substituted . It

is mostly used to treat volatile chlorinated compounds by passing the heated gases containing the contaminants through layers of noble metal catalysts , triggering off a reductive reaction that destroys the halogen bond. An example of this may be given by the change of trichlorethylene into ethane.

Reductive dechlorination of organic compounds may also be accomplished by redox active soil components such as iron oxides or Fe (II) bearing clays. This is a low cost technology having a good effectiveness.

Reductive microbial dechlorination (KLASSON et. al, 1996) is a method combining the benefits of biotechnology with the known abiotic methods of dechlorination, by adding micro-organisms to the prepared beds where the remediation takes place. These (micro -organisms) enhance the process of dechlorination.

f) Soil vapour extraction (SVE)

Soil vapour extraction is a popular technology for remediation of soils. It is a relatively simple process to remove volatile and easily evaporated organic contaminants within the vadose zone i.e. contaminants persisting or accumulated above the ground water table. Technical processes of these technology comprise injecting clean air into the unsaturated zone to effect a separation of organic vapours from the soil solution by partitioning between the soil solution and the soil air. The vapours joining the soil air are then removed via vacuum extraction wells. Figure 106 shows a schematic view of an SVE- arrangement.

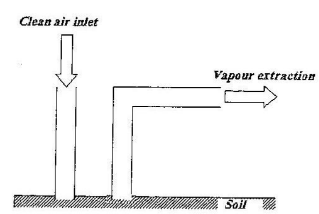

Fig. 106 .A schematic diagram to explain the technical arrangements required for soil vapour extraction (SVE)

It is needless to say that the effectiveness of soil vapour extraction will depend principally on the degree of water saturation in the treated soil as well as on the physical and chemical properties of the extracted contaminant such as vapour pressure and volatility.
Vapour extracted by this method may be further treated by carbon adsorption or any other suitable method that may help to dispose of the toxic gases collected.
To enhance the extraction in this technology, heated air or steam may be injected into the soil. Reports on using steam at sites of defunct gas stations show high efficiency performance at a reasonable low cost. Adding an air sparging system to the technical installations of SVE makes this technology also suitable for removing contaminants from the saturated zone.

g) Soil washing

In this technology polluted water is scrubbed by water and mechanical agitation to remove the hazardous contaminants or reduce their volume. It makes use of the selective binding of contaminants to fine material (silt and clay) rather than to coarse soil material such as sand and gravel. Adding chemical additives or surfactants to the water may enhance this process. After separating the two soil fractions, fine material carrying the major part of contaminants is further treated by other methods of remediation to get rid of the separated contaminants (see figure 107), while the coarse material if cleaned up may be returned to the plot.

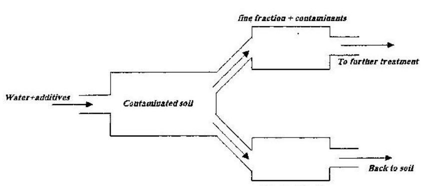

Fig. 107 . Schematic diagram showing the different steps in soil washing

Soil washing belongs to the category of **volume reduction techniques** in which the contaminants are concentrated in a relatively small mass of material. It is used to treat soils contaminated by a wide range of contaminants ranging from metals to oil products and pesticides.

h) Soil flushing

Soil flushing is a remediation method used for in situ treatment of inorganic and organic contaminants. Known sometimes as the cosolvent flushing method, this technique depends upon injecting a solvent mixture such as water and alcohol or surfactants into the vadose or saturated zone. The leachate i.e. the solvent with leached contaminants is drawn from recovery wells to be treated above ground or be disposed of. Flushing technique is used mainly to treat soils contaminated by inorganics including radioactive contaminants. It may also be used to treat VOC's, SVOC's, pesticides and fuel remnants. It must, however be mentioned that flushing may not be effective for soils with low permeability. Also the costs for aboveground treatment of the leachates may raise the financial burden of the remediation project. Fig. 108 is a diagrammatic Illustration of the process.

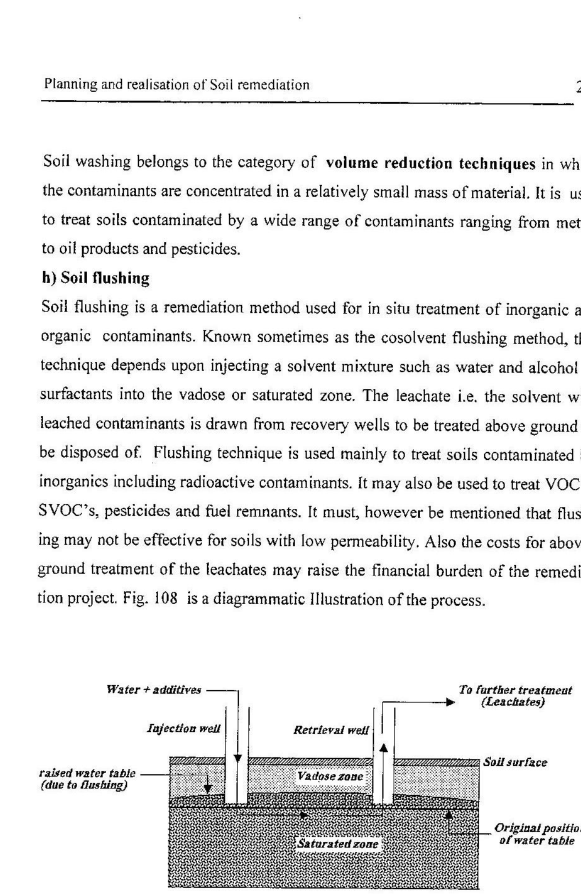

Fig. 108 .Diagrammatic illustration of soil flushing techniques

2. Biological treatment (Bioremediation)

Biological treatment of contaminated soils is a remedial technique making use of naturally occurring micro-organisms in the soil, that , are capable of degrading toxic materials , while carrying out their daily biological activities. Examples of such organisms may be given by bacteria or yeast. As explained before, some bacteria are capable of digesting a wide range of organic contaminants that other wise are very difficult to separate or degrade by any of the known technical methods.

It is an easy and effective method resulting in changing organic contaminants such as fuels or other oil products into carbon dioxide and water. However, the time required for complete remediation will depend upon whether the process is carried out in situ or in special facilities, where excavated soil material is transported. Ex situ technologies are normally faster and more effective than in situ processes.

a) In situ bioremediation techniques

In situ bioremediation techniques is mainly used to treat non halogenated semi volatile organics such as diesel fuel and heavy oils beside other materials that are susceptible to metabolism by micro-organisms. This technique -some times known as aerobic bioremediation- is accomplished by introducing oxygen and nutrients to the soil in order to enhance biodegradation of the contaminants. Two technical methods are used to create the suitable life conditions for the micro-organisms. These are:

1) **Bioventing** In this method atmospheric air is injected through special wells into the soil above the water table i.e. in the vadose zone, to supply the oxygen required for the micro-organisms.

2) peroxide injection: Here oxygen is introduced in a liquid form through injection of hydrogen peroxide into the soil. However this method is only applied to sites, where the ground water is already contaminated, in order to avoid unknown consequences resulting from contamination of the ground water by this chemical in areas of limited pollution.

b) Ex situ bio remedial methods

Ex situ bio remedial methods i.e. those methods carried out away from the pollution site are normally faster than the in situ methods. They are applicable for a wider range of contaminants, yet they are more expensive and may in some cases need pre treatment as well as post treatment measures in order to achieve highest Effectiveness. According to whether the treatment takes place in special tanks or in prepared beds , ex situ bio remediation comprises two main technologies – slurry phase treatment and solid phase remediation.

1) Slurry phase treatment: In this technology the polluted soil is excavated and transported to special facilities, where, it is mixed with water in special tanks (bio reactors). Oxygen and nutrients are later added, and the so formed mixture is thoroughly mixed to form a thin slur. Temperature, nutrients and oxygen concentrations are controlled so that the organisms may have the best conditions to sustain their bioactivities leading to the degradation of the pollutants.

2) Solid phase treatment : Here the polluted soil is treated above the ground in prepared beds. Despite the benefit of being less expensive than the slurry bed treatment, it is not so effective and needs more time and space to prepare the beds. Three main techniques are commonly used to carry out this remediation method – land farming, soil biopiles and composting.

a) Land farming:

The soil is excavated and spread on a pad with a built in system for collecting any possible leachates seepage. The so-formed bed is regularly mixed and turned over in order to facilitate aeration and enhance biological activity in the bed. Nutrients are added if required, since lack of nutrients and oxygen may lead to retardation of the bio degradation processes.

b) Soil biopiles The excavated soil is heaped in piles of several meters height. To enhance degradation activities by the microorganisms, air is blown through the pile. If required, nutrients are also added. Due to emissions from the piles, the whole process is sometimes carried out in inclusions that control any volatile contaminants.

c) Composting

Composting is an aerobic process during which organic matter is decomposed by microorganisms producing heat, carbon dioxide, water vapour and humus.

In the composting technique, biodegradable waste or contaminated soil is mixed with bulking materials such as straw to facilitate circulation of air and water required for the biological activities of the microorganisms. Nutrients are also added if required. Biodegradation of the waste or contaminants takes place some times in **static piles composting heaps,** where the soil is heaped in piles, that are periodically aerated with blowers or vacuum pumps. It may also be carried out in **mechanically agitated special tanks,** where aeration takes place through agitation..

Another technique through which composting may be carried out is the one known as **window composting**. In this technique soil is spread in long piles , exposed to atmospheric air and photolytic effects of sun light. Organic matter degradation by micro-organisms takes place in these heaps assisted by atmospheric oxygen and humidity.

Figure 109 shows in a schematic way the most common processes in biological treatment of polluted soils and the relations that connect them. Metabolic processes and enzymatic reactions were already explained in chapter 9.

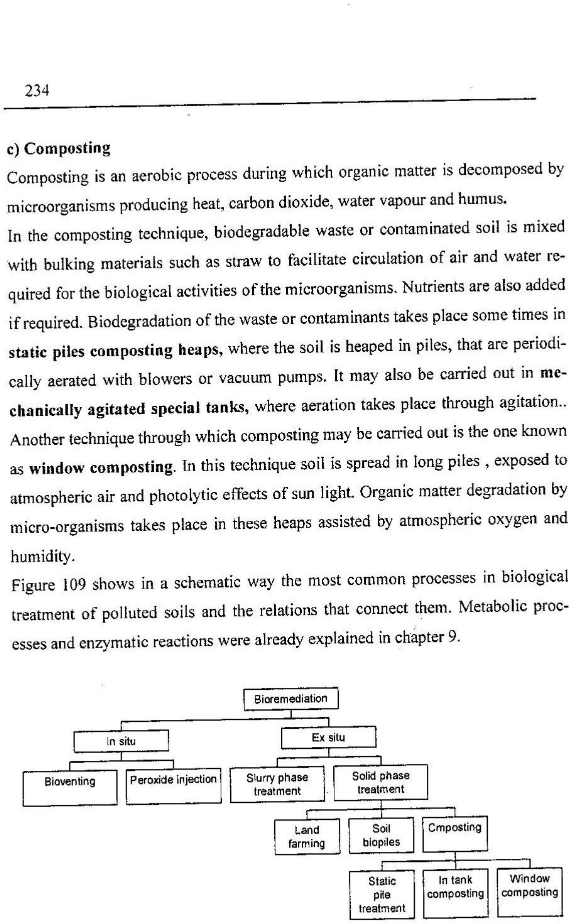

Fig. 109A schematic diagram showing the different technologies of bioremediation

Phytoremediation (Vegetation-assisted bioremediation)

Phytoremediation is a passive technology of soil remediation which has been gaining increasing popularity in the last decades. It depends on using plants (phyto) to remove, break down or stabilize contaminants in moderately shallow polluted sites. In such sites metals are stabilised or removed from the soil when taken up by the plants. Phyto remediation functions through different biological functions, depending upon the chemistry and nature of the soil pollutants.

Plants remove metal contaminants from the soil by two main processes, known as phytoextraction and rhizofilteration:

a) Phytoextraction (phytoaccumulation): Plants absorb metals from the soil by means of their roots and transport them to other plant parts, where they may be accumulated. Accordingly plants known to possess the ability of absorbing metals are chosen and grown on soils contaminated by metals or their salts. After sometime the plants are harvested and are either incinerated or recycled by composting or any other suitable method.

b) Rhizofilteration:

Rhizofilteration is a process through which a well developed root system is used as a filter for metals. This process takes place more readily in water than in soil and that is why it is mainly used to extract metals or radioactive matter from water. Other than in the phytoextraction process, here only the roots, where the metal accumulation has taken place, are harvested and disposed of. Two main steps are characteristic for this method, first the plants are grown in green houses until the root system is well developed and then replacing the water in the tanks, where the plants are grown by the contaminated water. The plants then take up the water and the contaminants along with it.

In case of treating soils contaminated with organic substances, four processes have been observed:

a) Phytodegradation
b) Enhanced rhizosphere biodegradation
c) Organic pumps
d) Phytovolatilisation

a) Phytodegradation

In this process plants are capable to degrade or break down organic contaminants. This occurs mainly through enzymatic reactions. Some of these reactions were explained in length in chapter 9 of this book.

b) Enhanced rhizosphere biodegradation

In this process plants work hand in hand with soil microorganisms in order to breakdown organic pollutants. Microorganisms carrying out biodegradation of the polluting material are supported by the root system (rhizosphere) that produces nutrients (e.g. alcohols, sugars) needed for the energy requirements of the organisms. This cooperative process keeps the microorganisms at a level sufficient for them to carry out their life activities and secure a continuous degradation of the toxic contaminants.

c) Organic pumps

Some trees (e.g. Poplar trees, cotton woods) are capable of pulling out big volumes of underground water, so that they may be compared with pumps continuously pumping water out of the soil. This action decreases the tendency of contaminants to penetrate the saturated zone and reach the ground water.

d) Phytovolatilisation

This occurs mainly in trees taking up a great deal of water containing organic contaminants. The contaminants may evaporate or leave the plant system via evapotranspiration.

Figure 110 shows in a schematic way the different processes observed in phytoremediation and the relations between them.

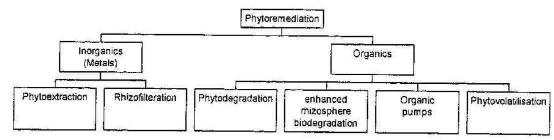

Fig. 110 . Summary of the different phytoremediation processes

3. Solidification / stabilisation methods

This is a group of technologies aiming at immobilising or stabilising contaminants in the soil and preventing them from entering the environment either by enclosing them into a solid mass or converting them to the least soluble , mobile or toxic form. Various technologies are known that secure safe performance of these processes. The following are the most successful among them.

a) Bitumen- based solidification

In this technology, the contaminated material is embedded in molten bitumen and left to cool and solidify. The contaminants thus encapsulated in the molten bituminous mass are changed to an immobile form that cannot enter the environment.

b) Encapsulation in thermoplastic materials

Thermoplastic materials (e.g. Modified sulphur cement) are molten and mixed with the contaminated material in special tanks and vigorously mixed to form a homogenous slurry fluid. After cooling the resulting solid may safely be disposed of.

c) Polyethylene extrusion

The contaminated soil is mixed with polyethylene binders, heated and then left to cool. The resulting solid may be disposed of or used in other ways.

d) Pozzolan / Portland cement

Pozzolanic-based materials (e.g. fly ash, kiln dust, pumice) are mixed with the contaminated matter in presence of water and alkali additives. At this environment heavy metals may precipitate out of the slurry. The rest mass solidifies enclosing the remaining organic contaminants.

e) Vitrification

In this process the contaminated soil is encapsulated into a monolithic mass of glass. Vitrification may be carried out in situ or ex situ. Introducing graphite electrodes into the soil and heating it electrically by powerful generators to temperatures between 1600-1800 °C perform in situ Vitrification. At these temperatures the soil melts and forms a glass block on cooling. Organic contaminants are pyrolysed and reduced to gases during the melting process, while heavy metals remain enclosed in the stabilised glass mass. This method has also been successfully used in treating soils contaminated by radioactive materials.

Vitrification may also be done in special appliances where contaminated soil would be molten in presence of borosilicate and soda lime to form a solid glass block.

4. Thermal treatment

Volatilisation and destruction of contaminants by thermal treatment is a very effective technique . It is achieved by heating the contaminated soil in kilns to temperatures between 400 and 700 °C, followed by further treatment of the kiln off gas at higher temperatures(800- 1200°C) to secure total oxidation of the organic volatile matter. Thermal treatment comprises various technologies, the most important of which are :

a)Incineration

In this technology Contaminants are combusted at high temperatures (970°C – 1200 °C) . It is particularly effective for halogenated and other refractory organic pollutants. Properly operated incinerators may be of very high destruction and re-

moval efficiency (DRE) reaching to as much as 99.9999 %, which is normally required for PCB's and dioxins.

b) Thermal desorption

This is the process by which organic contaminants are volatilised under controlled conditions by heating the contaminated soil to temperatures up to 600°C.Under these conditions, contaminants of low boiling points vaporise to be afterwards collected and further treated. Other than incineration, this technology aims to physically separate the contaminants from the soil.(Fig.111)

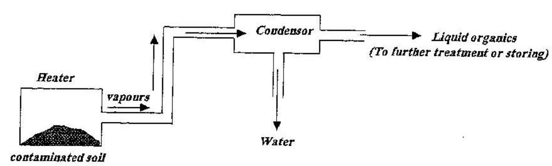

Fig. 111 Schematic diagram of a Thermal desorption system

c) Plasma high-temperature metals recovery:

At high temperature (plasma activated) metal fumes are purged, and later recovered and recycled. This is suitable for soil as well as for ground water.