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OVERVIEW OF *EX SITU* DECONTAMINATION TECHNIQUES FOR SOIL CLEANUP

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Abstract

The paper is a short review on the soil decontamination applying *ex-situ* techniques. Some sources and pathways of soil contamination are discussed. It was revealed that available techniques for soil decontamination can be divided in two parts, depending on where the action have place: *in-situ* or *ex-situ*. Also, depending on the nature of the process, these techniques can be biological, physical-chemical and thermal. In order to decontaminate soils properly, the primary contaminants (hydrocarbons such as petroleum residues, solvents, pesticides, herbicides, wood preservatives, heavy metals, munitions, which result from different industries and agricultural activities) have to be detected and analyzed.

The main features of *ex-situ* soil decontamination are reviewed and also status of each technology, advantages, disadvantages, limitations, and contaminants treated, are included.

Keywords: contaminant, *ex-situ*, remediation, soil

1. Introduction

The soil is a very unique part of the natural and agricultural aspects of the terrestrial ecosystem given its role in the growth of plants and the degradation and recycling of dead biomass. It is heterogeneous in nature and often comprises mineral and organic solids, aqueous and gaseous components (Alloway, 1995; Edwards and Stinner, 1988; Hyman and Dupont, 2001).

The mineral component of soils often consists of weathering product of rock parent materials and secondary minerals such as phylosilicates, or clay minerals oxides of Fe, Al, and Mn and sometimes carbonates such as $CaCO_3$. Living organisms (mesofauna and microorganisms), dead plants and colloidal humus formed by the action of microorganisms on plant litter make up the organic matter component of the soil. These solid components are usually clustered together in the form of aggregates, thus creating a system of interconnected pores (voids) of various sizes filled with either water

or air (Alloway, 1995; Gavrilescu, 2006; Gavrilescu et al., 2008).

The resulting soil-water-air environment is very complex. This is because different soil fractions and constituents give rise to different reactions when anthropogenic chemicals are introduced. In many cases, contaminants become bonded, especially to clay and or organic materials and are hence unavailable to present future risks (Schacht and Ajibo, 2002). In other situations however, the anthropogenic chemicals may remain un-bonded, or could be remobilized by changes in soil acidity or redox potential and becomes far more able to create risk (Gavrilescu, 2006, Mirsal, 2008).

Many pesticides have been converted to 'bound residues' in soil (Alexander, 1999; Dankwardt and Hock, 2001). Most of the complexes formed is with the organic or humus fraction of the soils, and probably usually involves the formation of covalent bonds between the compound and the humic material. The complexes are assumed to be formed either by an attachment of the compound to reactive sites on the surfaces of the organic colloids or by incorporation of

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the compound into the structure of the humic or fulvic acids that are being formed microbiologically (Stevenson, 1976; Worsztynowicz et al., 2008).

The goal of a remediation effort is to limit the extent of contamination at a hazardous waste site, to prevent further deterioration of the environment and to prevent exposure by humans and other life forms to hazardous chemicals. The remedies at a given site vary depending on the properties of the chemicals found at the site, the t

ypes of soils, and the depth of contamination, and natural processes that may occur at the site (Mirsal, 2008). The criteria for selecting remediation technologies or treatments are (Cheremisinoff, 1998; Gavrilescu, 2006; Lodolo et al., 2001; Rao et al., 2002; Vik et al., 2001):

• Short-term and long-term effectiveness at meeting the remediation goals

• Reduction in the volume of contaminants most effectively

• Reduction in the toxicity of contaminants

• Cost effectiveness.

Other factors affect the choice of remedies-for example, land disposal of hazardous materials is restricted under present environmental regulations. Because a variety of remedies can often control contamination at hazardous waste sites, selecting the appropriate technology or technologies can be a challenge.

The following categories of remedies are listed in order from least disruptive, intensive and expensive to most disruptive, intensive and expensive (EPA, 2008; GFG, 2002; Hyman and Dupont, 2001; Pare, 2006):

1) **Do nothing**. If the environmental assessment indicates that humans and the environment are not at risk, then no remediation activity is required. "Do nothing" may be deemed the appropriate action for small-scale spills on sites where human and animal exposure is not likely.

2) **Institutional Controls (IC)** - institutional controls are legal or institutional mechanisms that limit access to or use of property, or warn of a hazard. An IC can be imposed by the property owner, such as use restrictions contained in a deed or by a government, such as a zoning restriction. At contaminated sites, institutional controls are used to prohibit access to the contaminated areas. Examples of institutional controls include fencing off a contaminated site or prohibiting the construction of wells near polluted aquifers.

3) **Monitored Natural Attenuation** - In some cases nature promotes cleanup of contamination. Some contaminants may be broken down into safe elements via sunlight (known as photolysis), natural bioremediation, and chemical reactions (such as hydrolysis). Contaminants can also "stick" (or sorb) to soil or other solid particles, limiting the mobility of contaminants in the soil.

4) **Containment of Contaminants** - The risk of environmental contamination can be reduced by limiting the ways that humans, wildlife or the environment can come in contact with the contaminants. Methods include capping of soils with clean material, creating physical barriers, and stabilizing or solidifying contaminants in place. Containment of contaminated groundwater is more difficult and may involve elaborate and often expensive pumping and treatment systems.

5) **Destruction of contaminant** - Destroying the contaminants may remove the risk posed by contaminants if the by-products are not toxic. Treatments can be in situ (in place) or ex situ (after excavation of the soil or pumping of the ground water from the aquifer). Technologies include phytoremediation, bioremediation, Fenton's Reagent and ozonization.

6) **Removal** - In some cases, the best option may be to physically remove the contaminated soil and move it to a permitted Treatment, Storage and Disposal Facility (TSDF). This is especially true with soils that are contaminated with both chemicals and radioactivity. In other cases, it is possible to remove the contaminant from the soil using such technologies as surfactant washing, soil washing or thermal desorption. Contaminants in groundwater can be removed using pump-and-treat technologies involving methods such as activated carbon or ion exchange.

The soil is a structure that is stratified. The upper layer is the unsaturated zone (or infiltrating zone), below which we have the saturated zone. There are many characteristics of the soil that influence the transport of contaminants, such as: density, porosity, humidity and permeability. This phenomenon is also influenced by some properties of the contaminants, such as vapor pressure and chemical nature (Norris, 1994). After identifying the type of soil and the nature of the contaminants, a suitable remediation technique must be chosen, and the effectiveness of the decontamination process evaluated (Castelo-Grande and Barbosa, 2003; Hyman and Dupont, 2001).

The existing methods for soil decontamination may be divided in: "in situ" techniques, "ex situ" techniques, and the confining/isolation of the contaminated area, which is a temporary solution. These methods can be further divided in biological and non-biological methods. The non-biological methods are subdivided in physical-chemical methods, thermal methods and others methods (e.g., supercritical extraction and electrokinetic) (Castelo-Grande et al., 2003). In Tables 1 and 2 some of the existing decontamination techniques are summarized, and some of their advantages and disadvantages are given (FRTR, 2000; Hyman and Dupont, 2001).

2. *Ex-situ* biological treatment

One of the main advantages of ex-situ bioremediation is that it requires less time than the in-situ treatment. Another advantage is the certainty of the control treatment due to the ability to uniformly screen, homogenize and mix the soil.

Table 1. Advantages and disadvantages of some biological technologies used in soil remediation (Castelo-Grande et al., 2003).

Technology	Advantages	Disadvantages
Landfarming	-Relative simple design and implementation; -Short treatment times (six months to two years under optimal conditions).	-Reductions of concentration greater than 95% and concentrations lower than 0.1 ppm are difficult to achieve; -The required area is high; -Dust and vapor generation during landfarming aeration may cause some air quality problems.
Bioventing	-Uses readily available equipment, easy to install; - Creates minimal disturbance to the treatment site; -May not require costly off gas treatment; -Easily combinable with other technologies (e.g., air sparging, oundwater extraction).	-The high concentrations may be toxic for microorganisms; -Not applicable for certain site conditions (e.g., low soil permeability); -Sometimes requires nutrients and air injection wells; -Only treats unsaturated zones of soils, and needs other methods to treat saturated zones of soils and groundwater.
Natural attenuation	-The generation of less remediation waste, and less impact on the environment; -Ease to use when combined with other technologies; -No equipment down time.	-The public may not perceive the effectiveness of the process correctly; -Site characterization can be more costly and complex; - Due to monitoring, active remediation may be more economical; -The potential exists for continued migration.
Phytoremediation	-Is much less expensive than conventional options.	-Is a technology that is seasonal; - Only applicable to low profundity.
Biosparging	-Readily available equipment; -Cost competitive; -Requires no removal, treatment, storage or discharge of groundwater.	-Some interactions among complex chemical, and physical and biological processes are not well understood; -Potential for inducing migration of constituents.
Bio – Rehabilitation in-situ	-Degradation of material dissolved in infiltrated and saturated zone; -Equipment easily available.	-The hole can be obstructed by biomass or precipitation; -Continuous monitoring and maintenance.

Table 2. Advantages and disadvantages of some non-biological technologies used in soil remediation (Castelo-Grande et al., 2003)

Technology	Advantages	Disadvantages
Vitrification (Thermal)	-Ex situ vitrification is a well developed technology; -The mobility of contaminants is reduced/eliminated; -The vitrified mass resists leaching for geologic periods of time.	-The process requires intensive energy and high temperatures up to near 2000 K; -Water in soil affects operation and increases the total costs of the process; -Off gases must be collected and treated before release; -In situ vitrification is in pilot scale development.
Incineration (Thermal)	-Contaminant toxicity, as well as volume reduction is addressed by this technology. This is specially true for organic contaminants; -Widely used and available commercially.	-Metals are not destroyed and end up in the flue gases or in the ashes; -Community resistance to incineration is often present; -Certain types of soils such as clay soils or soils containing rocks may need screening.
Soil Washing (Physical-Chemical)	-Reduces the volume of contaminant, therefore, further treatment or disposal is less problematic; -Commercially available.	-Contaminant toxicity is unchanged, although volume is reduced; -Less effective when soil contains a high percentage of silt and clay; -Costs associated with the disposal of

		the subsequent waste streams must be considered.
Soil Vapour Extraction (physicalchemical)	- Proven performance, readily available equipment, easy to install; - Minimal disturbance to site operations; -Short treatment times (6-48 months).	-Concentration reductions greater than 90% are difficult to achieve; -Effectiveness decreases when applied to sites with low permeability; -Only treats the unsaturated zone; -May require costly treatment for atmospheric discharge of the extracted vapor.
Electrokinetic (others)	-In situ technology that has small impact on environment (soil removal is not required). -Metals are actually removed from soil unlike stabilization, which leaves the metals in the soil.	-Alkaline soils reduce the effectiveness of the process; -Requires soil moisture.

These factors have made this one of the most commonly used treatment technologies (EPA, 1993b; Mirsal, 2008). However; *ex-situ* bioremediation involves the excavation and the treatment of the contaminated soil somewhere else, which makes it less cost-effective (Donlon and Bauder, 2008; Pare, 2006; Schacht and Ajibo, 2002).
Ex-situ treatment technology is further divided into slurry-phase bioremediation and solid-phase bioremediation.

2.1. Slurry-phase Bioremediation

Slurry-Phase bioremediation, also known as bioreactors, is a controlled treatment that involves the excavation of the contaminated soil, mixing it with water and placing it in a bioreactor. Fig. 1 shows a typical bioreactor system (FRTR, 2000).

As shown in the figure, the process requires the processing of the soil to provide a low viscosity. This processing involves the separation of stones and rubbles from the contaminated soil. Next, the soil is mixed with a predetermined water amount to form the slurry. The concentration of water added depends on the concentration of pollutants, the rate of biodegradation, and the physical nature of the soil (EPA, 2003; Hyman and Dupont, 2001).

When this process is done the soil is removed and dried up using pressure filters, vacuum filters or centrifuges. The next procedure is the disposition of the soil and further treatment of the resulting fluids.
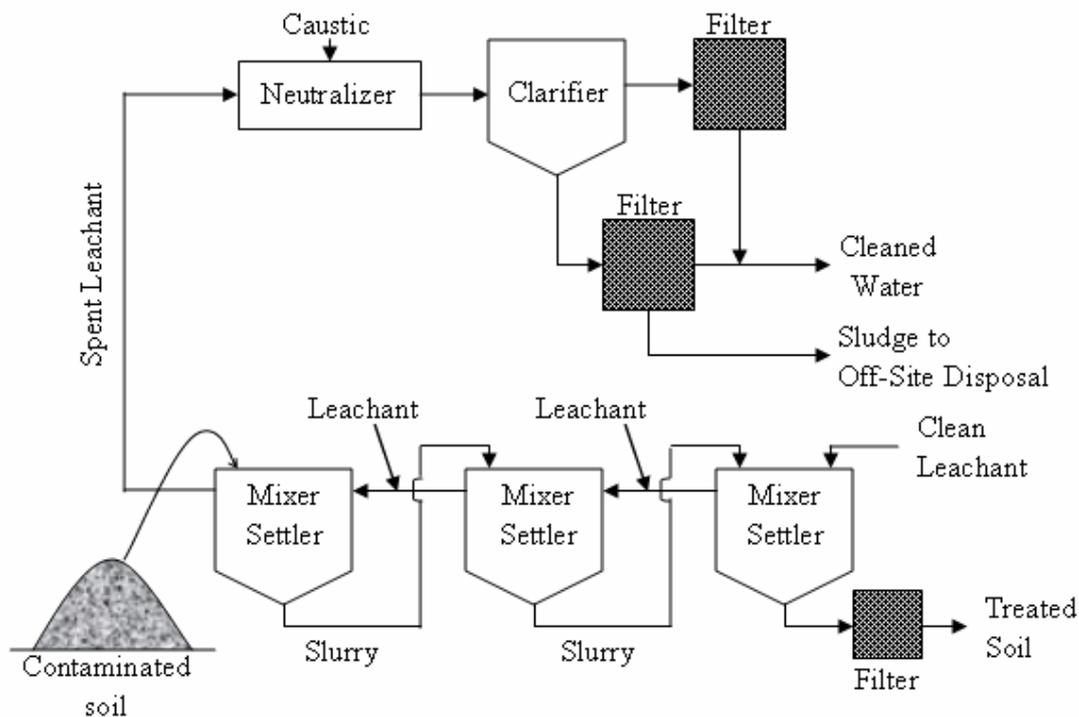
Fig. 1. Bioreactor system (FRTR, 2000)

2.2. Solid-phase bioremediation

Solid-Phase bioremediation is an ex-situ technology in which the contaminated soil is excavated and placed into piles. Bacterial growth is stimulated through a network off pipes that are distributed throughout the piles (Hyman and Dupont, 2001). By pulling air through the pipes the necessary ventilation is provided for microbial respiration.

Moisture is introduced by spraying the soil with water. Solid-phase systems require a large amount of space, and cleanups require more time to complete than with slurry-phase processes (EPA, 2001). Some solid-phase treatment processes include land farming, soil biopiles, and composting.

2.2.1. Landfarming

Landfarming, also known as land treatment, is a bioremediation technique that involves the excavation of the contaminated soil and spreading it on a thin surface. Biodegradation of pollutants is stimulated aerobically by tilling or plowing the soil. Nutrients and minerals are also added to promote the growth of the indigenous species. Fig, 2 is a schematic representation of the landfarming system.

According to The Unites States Environmental Protection Agency (EPA) report on underground storage tanks (EPA, 2003), before the remediation takes place the site must be prepared by clearing and grading the soil, by installing leachate collection and treatment systems, and also building vapor treatment facilities.

Also, the report states that if a contaminated soil is less than three feet then there is no need for excavation.

As it can be seen in the figure, while soil moisture is controlled by periodically sprinkling soil with water, building barriers or terraces around the contaminated soil controls erosion.

Sprinkling with water also minimizes the dust created while tilling the soil to promote aeration (Rubinos et al., (2007).

2.2.2. Soil biopiles

Soil biopiles, also known as biocells, is a biodegradation technique used for the remediation of excavated soil contaminated with petroleum contents. This technology involves the accumulation of contaminated soil into piles and the stimulation of microbial activity either aerobically or by the addition of nutrients, minerals or moisture. A typical height of biopiles is between three and ten feet.

Biopiles are in a way similar to landfarms due to the fact that this technology also uses oxygen as a way to stimulate bacterial growth. However, while tilling or plowing aerates land farms, biopiles are aerated by forcing air to move by injection through perforated piping placed throughout the pile (EPA, 2003). A schematic of this technology can be seen in Fig. 3. As it can be seen in the figure, the contaminated soil is piled up to a depth of a few feet and then the piping, which provides aeration, is laid down. The next load of contaminated soil is then added. This process continues until the desired pile height is achieved. The soil is usually mixed with a bulking agent (straws) to improve aeration and therefore enhance the growth of the microbial population.
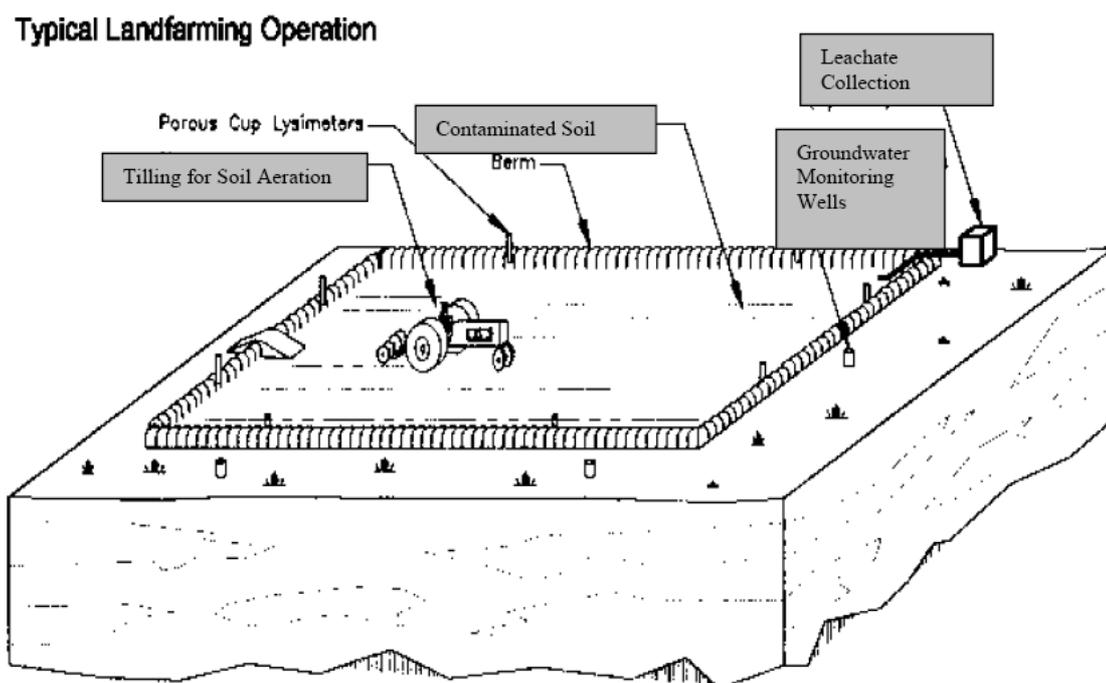
Fig. 2. Landfarming (FRTR, 2000)

Since air is also injected into the soil there is the possibility for evaporation or volatization of contaminants. To counter this problem, the system also includes the monitoring and containment of soil vapors.

2.2.3. Composting

Composting involves mixing the contaminated soil with a bulking agent such as straw, hay, or corncobs to make it easier to deliver the optimum levels of air and water to the microorganisms. The most common designs are static pile composting, mechanically agitated composting, and window composting.

In static pile composting the contaminated soil is placed into piles and aerated with blowers or vacuum pumps. Mechanically agitated composting involves the placement of the contaminated soil in treatment vessels where it is mixed to achieve aeration. In window composting, the soil is placed in long piles knows as windows and periodically mixed by tractors (Cunningham, 2000).

As stated before, the contaminated soil is mixed with a bulking agent or compost to enhance bacterial growth. A typical ratio of soil to compost is 75% contaminated soil to 25% compost. This ratio is changeable depending on the soil type, contaminants level and characteristics. After mixing, the soil is covered to protect it from erosion and to maintain the proper moisture and temperature necessary for bacterial growth.

Compost remediation is known to have faster cleanup results since cleanup can be estimated in terms of weeks instead of months.

2.3. Factors affecting biodegradation

A. Soil water

Water present in soil affects not only the moisture available to microorganisms, but also the soil aeration status, the nature and amount of soluble, osmotic pressure and the pH. Water activity in the soil is measured in terms of potential (matrix and osmotic). Matix potential is the capability of water to adsorb to solid surfaces. This potential is usually negative because it reduces the free energy of water. Osmotic potential in the other hand is related to solubility. Since water is a universal solvent, the presence of solute in the soil tend to also reduce the free energy of water and create another negative potential (Subhas and Irvine, 1998).

The sum of osmotic and matrix potentials describe the water availability, and as a result will define how much energy must a microorganism spend to obtain water. Microbial activity is known to have maximum reaction rates at water potentials of -0.01Mpa (megapascals); however, these rates tend to decrease if the soil becomes either waterlogged (near zero Mpa) or drier, at negative water potentials. Fig. 4 shows the relation between water potential and bacterial reaction rates.

B. Redox Potential

Bacteria obtain their energy from oxidation and reduction of compounds present in the soil by removing electrons from these compounds in order to obtain the energy available during the oxidation process.
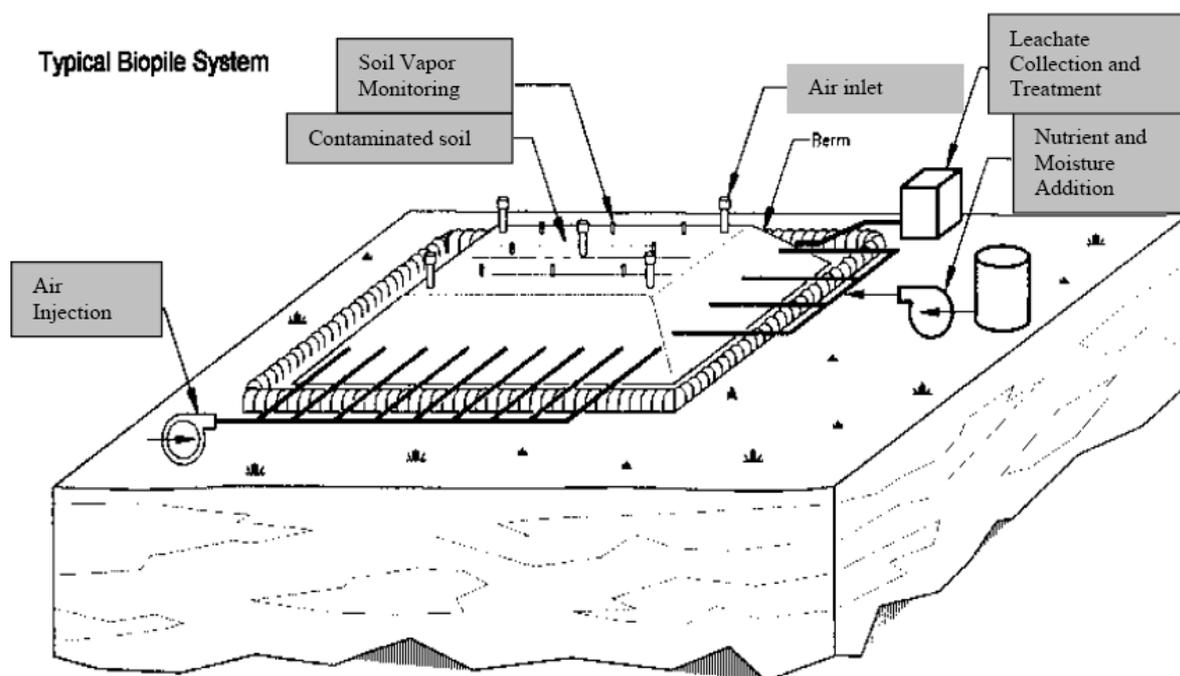
Fig. 3. Biopile system (FRTR, 2000)
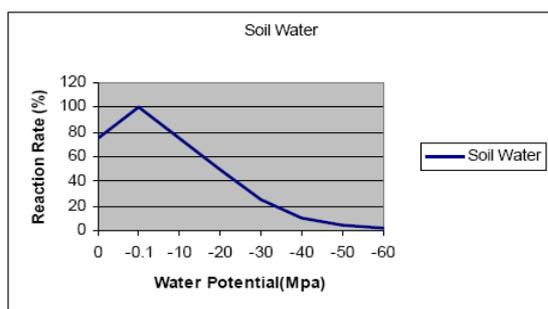
Fig. 4. Relation between water potential and bacterial reaction rates (Subhas and Irvine, 1998)

This process depends largely on a compound that can accept electrons. When talking about aerobic degradation the final electron acceptor is oxygen.*C.*

C. Soil pH
Soil pH values are somewhat related to the size of the organisms present and the multiplicity of enzymes at the microbial level (Schacht and Ajibo, 2002). Bacteria tend to have optimum pH between 6.5 and 7.5, which equals the intracellular pH. The biodegradation of a compound is dependent on specific enzymes, which are secreted by the organisms. These enzymes are largely pH dependent (Singh et al, 2003; Hyman and Dupont, 2001).

D. Soil temperature
Temperature is one of the major factors affecting the biodegradation of a toxic compound. It not only affects the rates of biochemical reactions in the organisms, but also the soil moisture, and redox potential. All microbial activities are dependent upon the laws of thermodynamics. At too high temperatures there is a denaturizing of the proteins and the cell membrane permeability. It is generally known that metabolism tends to slow down at low temperatures; however, psychrophiles, bacteria which grow in cold temperatures, are capable of degrading contaminants due to osmotic regulations and cytoplasma constituents that prevent the bacteria's cell interior from freezing. Fig. 5 shows the bacterial response to temperature variations.

3. *Ex-situ* physical/chemical treatment

Available *ex-situ* physical/chemical treatment technologies include (EPA, 1993a ; FRTR, 2000 ; Gavrilescu, 2006):
- chemical reduction/oxidation
- dehalogenation
- soil washing
- fluid vapor extraction
- stabilization/solidification
- solvent extraction

3.1. Chemical reduction/oxidation
Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to

nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another (Wang and Li, 2007). Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons) (FRTR, 2000; Pare, 2006).
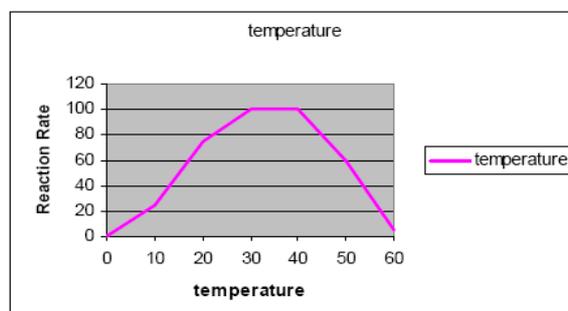
Fig. 5. Temperature vs. chemical reactions (Subhas and Irvine, 1998)

Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds. Oxidants are generally non-specific and will react with the targeted contaminants and with the soil organic content (Pare, 2006). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide wastes (Fig. 6.). Enhanced systems are now being used more frequently to treat contaminants in soils (EPA, 1991). The target contaminant group for chemical redox is inorganics. The technology can be used but may be less effective against nonhalogenated VOCs and SVOCs, fuel hydrocarbons, and pesticides (Mayer et al., 1990).
Factors that may limit the applicability and effectiveness of the process include:
- incomplete oxidation or formation of intermediate contaminants may occur depending upon the contaminants and oxidizing agents used.
- the process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required.
- oil and grease in the media should be minimized to optimize process efficiency.

3.2.1. Dehalogenation (base – catalyzed decomposition (BCD))
The dehalogenation [base -catalyzed decomposition (BCD)] process was developed by EPA's Risk Reduction Engineering Laboratory (RREL), in cooperation with the National Facilities Engineering Services Center (NFESC) to remediate soils and sediments contaminated with chlorinated organic compounds, especially PCBs, dioxins, and furans.
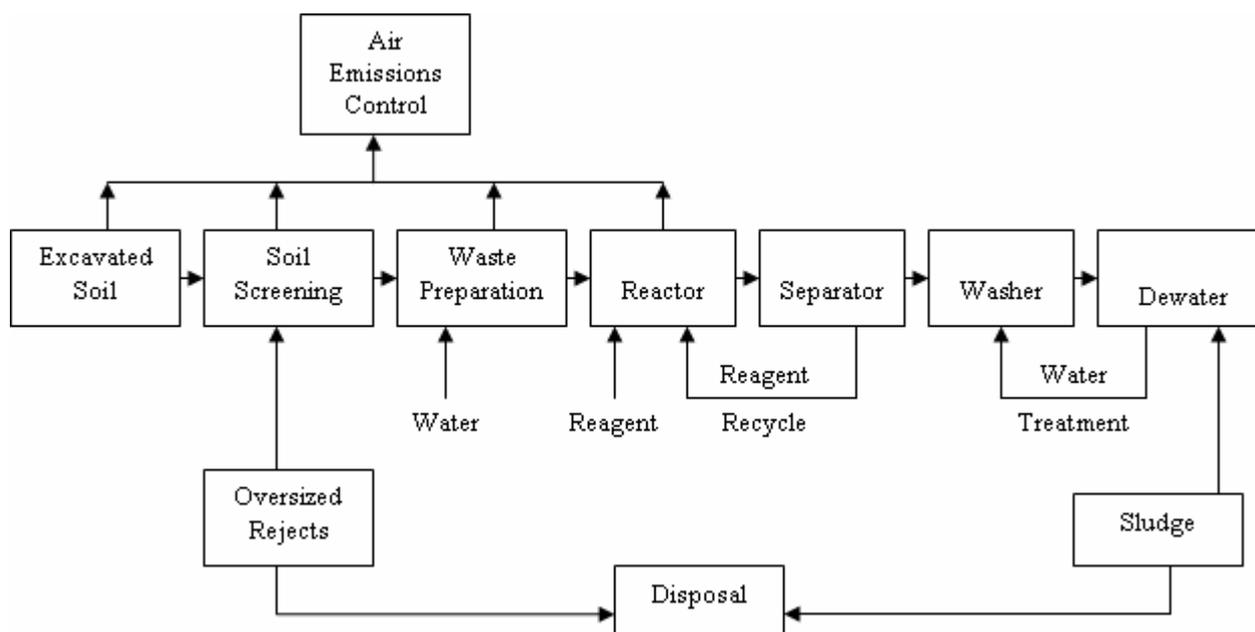
Fig. 6. Schematic representation of Chemical Reduction/oxidation process
(http://www.frtr.gov/matrix2/section4/D01-4-16.gif)
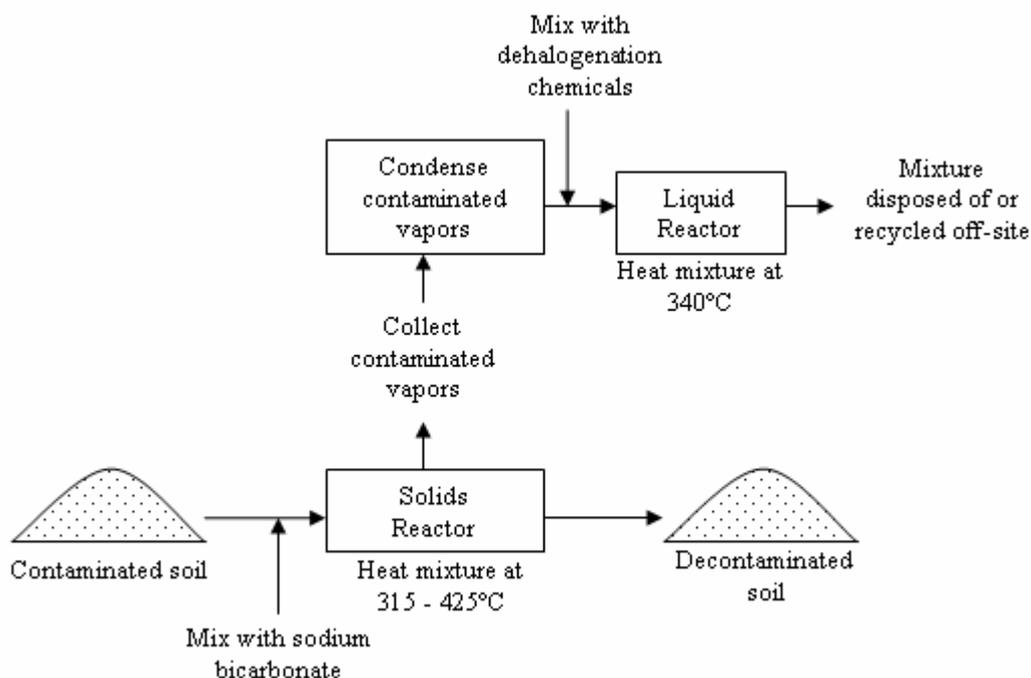
Fig. 7. Dehalogenation (base – catalyzed decomposition (BCD)) process

Contaminated soil is screened, processed with a crusher and pug mill, and mixed with sodium bicarbonate. The mixture is heated to above 330ºC in a rotary reactor to decompose and partially volatilize the contaminants, as it is shown in Fig. 7 (EPA, 1992).

The contaminant is partially decomposed rather than being transferred to another medium. Whereas alkaline polyethylene glycol (APEG)

residuals contain chlorine and hydroxyl groups, which make them water – soluble and slightly toxic, the BCD process produces primarily biphenyl and low-boiling point olefins, which are not water – soluble and are much less toxic, and sodium chloride (Donald et al., 2007).

The target contaminant groups for dehalogenation (BCD) are halogenated SVOCs and pesticides. The technology can be also used to treat

halogenated VOCs but will generally be more expensive than other alternative technologies.

The applicability and effectiveness of the process can be limited by high clay and moisture content will increase treatment costs.

3.2.2. Dehalogenation

Dehalogenation is a full-scale technology in which an alkaline polyethylene glycol (APEG) reagent is used to dehalogenate halogenated aromatic compounds in a batch reactor (Fig. 8) (FRTR, 2000). Potassium polyethylene glycol (KPEG) is the most common APEG reagent. Contaminated soils and the reagent are mixed and heated in a treatment vessel. In the APEG process, the reaction causes the polyethylene glycol to replace halogen molecules and render the compound nonhazardous or less toxic (EPA, 1990). For example, the reaction between chlorinated organics and KPEG causes replacement of a chlorine molecule and results in a reduction in toxicity. Dehalogenation (APEG/KPEG) is generally considered a standalone technology; however, it can be used in combination with other technologies. Treatment of the wastewater generated by the process may include chemical oxidation, biodegradation, carbon adsorption, or precipitation (Soesilo and Wilson, 1997).

The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG) (typically, average molecular weight of 400) to form a polymeric alkoxide referred to as KPEG.

Sodium hydroxide has also been used in the past, however, and most likely will find increasing use in the future because of patent applications that have been filed for modification to this technology. This new approach will expand the technology's applicability and efficacy and should reduce chemical costs by facilitating the use of less costly sodium hydroxide.

A variation of this reagent is the use of potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as ATEG, that is more effective on halogenated aliphatic compounds. In some KPEG reagent formulations, dimethyl sulfoxide (DMSO) is added to enhance reaction rate kinetics, presumably by improving rates of extraction of the haloaromatic contaminants.

Previously developed dehalogenation reagents involved dispersion of metallic sodium in oil or the use of highly reactive organosodium compounds. The reactivity of metallic sodium and these other reagents with water presented a serious limitation to treating many waste matrices; therefore, these other reagents are not discussed here and are not considered APEG processes. The reagent (APEG) dehalogenates the pollutant to form a glycolether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble byproducts.

The target contaminant groups for glycolate dehalogenation are halogenated SVOCs and pesticides. The technology can be used but may be less effective against selected halogenated VOCs. APEG dehalogenation is one of the few processes available other than incineration that has been successfully field tested in treating PCBs. The technology is amenable to small-scale applications.

Factors that may limit the applicability and effectiveness of the process include:
- the technology is generally not cost –effective for large waste volumes.
- media water content above 20% requires excessive reagent volume.
- concentrations of chlorinated organics greater than 5% require large volumes of reagent.

The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm.

Concentrations were reduced to less than 2 ppm per individual PCB congener. PCDDs and PCDFs have been treated to nondetectable levels at part per trillion sensitivity.
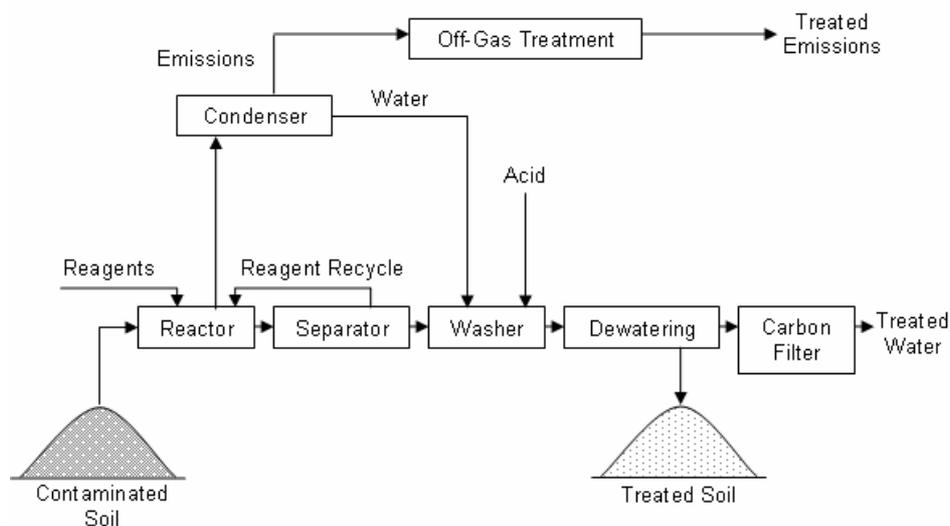
Fig. 8. Dehalogenation (glycolate) process

The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil. For a contaminated activated carbon matrix, direct treatment was less effective, and the reduction of PCDDs/PCDFs to concentrations less than 1 ppb was better achieved by first extracting the carbon matrix with a solvent and then treating the extract.

3.3. Soil washing

Soil washing is a water-based process for scrubbing soils ex situ to remove contaminants. The process, Figure 9, removes contaminants from soils in one of two ways:
• By dissolving or suspending them in the wash solution (which is later treated by conventional wastewater treatment methods).
• By concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing (similar to those techniques used in sand and gravel operations) (Raghavan et al., 1989).

Soil washing systems incorporating most of the removal techniques offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, radionuclides, and organic contaminants.

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion.

Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles, effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed off. Gravity separation is effective for removing high or low specific gravity particles such as heavy metal-containing compounds (lead, radium oxide, etc.). Attrition scrubbing removes adherent contaminant films from coarser particles. The clean, larger fraction can be returned to the site for continued use (EPA, 1992).

The target contaminant groups for soil washing are SVOCs, fuels, and inorganics. The technology can be used on selected VOCs and pesticides. The technology offers the potential for recovery of metals and can clean a wide range of organic and inorganic contaminants from coarse-grained soils. Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000; Raghavan et al., 1989):
- fine soil particles (e.g., silt, clays) may require the addition of a polymer to remove them from the washing fluid.
- complex waste mixtures (e.g., metals with organics) make formulating washing fluid difficult.
- high humic content in soil may require pretreatment.
- the aqueous stream will require treatment

Soil washing is most commonly used in combination with the following technologies: bioremediation, incineration, and solidification/stabilization. Depending on the process used, the washing agent and soil fines are residuals that require further treatment. When contaminated fines have been separated, coarse-grain soil can usually be returned clean to the site.

3.4. Ex-situ soil vapor extraction (SVE)

Ex situ soil vapor extraction (SVE), Fig. 10, is a full-scale technology in which soil is excavated and placed over a network of aboveground piping to which a vacuum is applied to encourage volatilization of organics (Hyman and Dupont, 2001).

The process includes a system for handling off-gases.
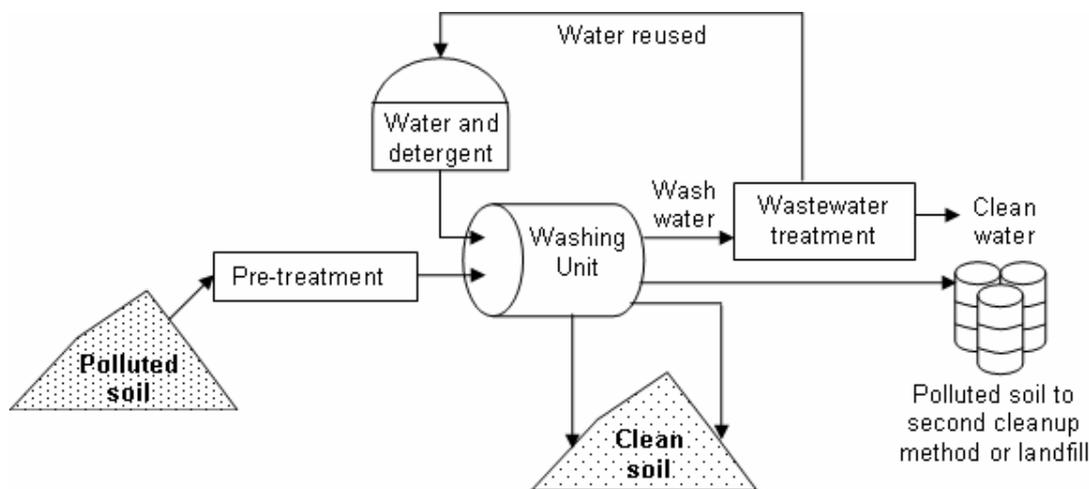
Fig. 9. Soil washing system

Advantages over its in situ counterpart include that the excavation process forms an increased number of passageways, shallow groundwater no longer limits the process, leachate collection is possible, and treatment is more uniform and easily monitored (EPA, 1990).
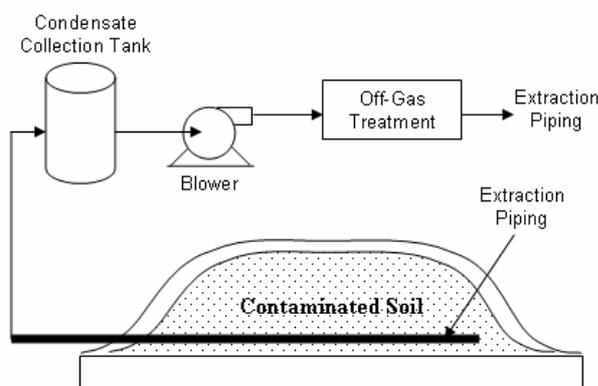
Fig. 10. *Ex-situ* soil vapor extraction (SVE) system

The target contaminant group for ex situ SVE is VOCs. The following factors may limit the applicability and effectiveness of the process (FRTR, 2000):

- air emissions may occur during excavation and materials handling, possibly requiring treatment.
- high humic content or compact soil inhibits volatilization.
- as a result of air emission treatment, SVE may require treating residual liquid and spent activated carbon, increasing the project cost.
- a large amount of space is required (Raghavan et al., 1989).

An advantage of the technology over its in situ counterpart is the increased number of passageways formed by the excavation process; however, as an ex situ remedy, the excavation associated with SVE poses a potential health and safety risk to site workers through skin contact and air emissions (James and Kovalick, 2001; Hyman and Dupont, 2001). Personal protective equipment, at a level commensurate with the contaminants involved, is normally required during excavation operations. The time required to remediate a site using ex situ SVE is highly dependent upon the specific soil and chemical properties of the contaminated media.

3.5. Solidification/stabilization

As for in situ solidification/stabilization (S/S), ex situ S/S contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization) (Bricka et al., 1988). Ex situ

S/S, however, typically requires disposal of the resultant materials (Fig. 11).
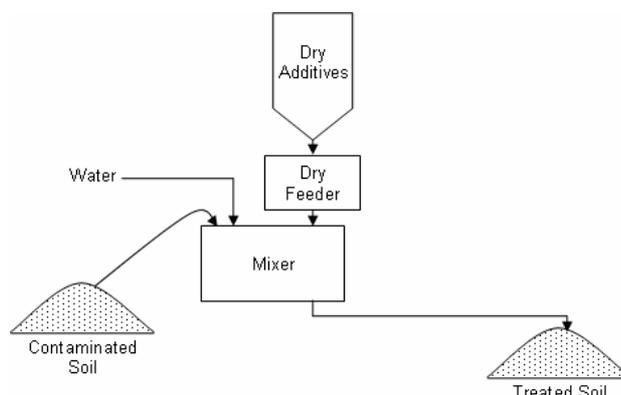
Fig. 11. *Ex-situ* solidification/stabilization

The target contaminant group for ex situ S/S is inorganics, including radionuclides. The technology has limited effectiveness against SVOCs and pesticides; however, systems designed to be more effective against organic contaminants are being developed and tested (Swarnalatha et al., 2006).

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- Environmental conditions may affect the long-term immobilization of contaminants.
- Some processes result in a significant increase in volume (up to double the original volume).
- Certain wastes are incompatible with different processes. Treatability studies are generally required.
- VOCs are generally not immobilized.
- Long-term effectiveness has not been demonstrated for many contaminant/process combinations (Raghavan et al., 1989).

Depending upon the original contaminants and the chemical reactions that take place in the ex situ S/S process, the resultant stabilized mass may have to be handled as a hazardous waste. For certain types of radioactive waste, the stabilized product must be capable of meeting stringent waste form requirements for disposal (e.g., Class B or Class C low level materials) (EPA, 1993a).

3.6. Solvent extraction

Solvent extraction does not destroy wastes but is a means of separating hazardous contaminants from soils, sludges and sediments, thereby reducing the volume of the hazardous waste that must be treated. The technology uses an organic chemical as a solvent and differs from soil washing, which generally uses water or water with wash-improving additives (Raghavan et al., 1988). Commercial scale units are in operation; they vary in regard to the solvent employed, type of equipment used, and mode of operation.

Solvent extraction is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing, depending upon site-specific conditions. It also can be used as a standalone technology in some instances. Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration. The treated media are usually returned to the site after having met Best Demonstrated Available Technology (BDAT) and other standards.

Solvent extraction has been shown to be effective in treating sediments, sludges and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. The technology is generally not used for extracting inorganics (i.e., acids, bases, salts, or heavy metals). Inorganics usually do not have a detrimental effect on the extraction of the organic components, and sometimes metals that pass through the process experience a beneficial effect by changing the chemical compound to a less toxic or leachable form. The process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood – treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes (EPA, 1990).

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- organically bound metals can be extracted along with the target organic pollutants, which restrict handling of the residuals.
- the presence of detergents and emulsifiers can unfavorably influence the extraction performance.
- traces of solvent may remain in the treated solids; the toxicity of the solvent is an important consideration.
- solvent extraction is generally least effective on very high molecular weight organic and very hydrophilic substances.

- some soil types and moisture content levels will adversely impact process performance.

4. Ex-situ thermal treatment

Ex situ thermal treatment generally involves the destruction or removal of contaminants through exposure to high temperature in treatment cells, combustion chambers, or other means used to contain the contaminated media during the remediation process (http://www.clu-in.org/techfocus/default.focus/sec/Thermal_Treatment:_Ex_Situ/cat/Overview/). It includes:

- hot gas decontamination
- incineration
- open burn/open detonation
- pyrolysis
- thermal desorption
- Ex-situ Vitrification

4.1. Hot gas decontamination

The process involves raising the temperature of the contaminated equipment or material to 260ºC for a specified period of time. The gas effluent from the material is treated in an afterburner system to destroy all volatilized contaminants (Fig. 13). The method eliminates a waste that currently is stockpiled and requires disposal as a hazardous material. This method will permit reuse or disposal of scrap as nonhazardous material (Topfer, 1995).

Consideration is being given to applying the hot gases to explosives – contaminated underground piping in situ. Hot gas decontamination can also be used for decontamination of explosives – contaminated masonry or metallic structures.

The method involves sealing and insulating the structures, heating with hot gas stream to 260ºC for a prescribed period of time, volatilizing the explosive contaminants, and destroying them in an afterburner. Operating conditions are site – specific. Contaminants are completely destroyed (Hyman and Dupont, 2001; Raghavan et al., 1989).
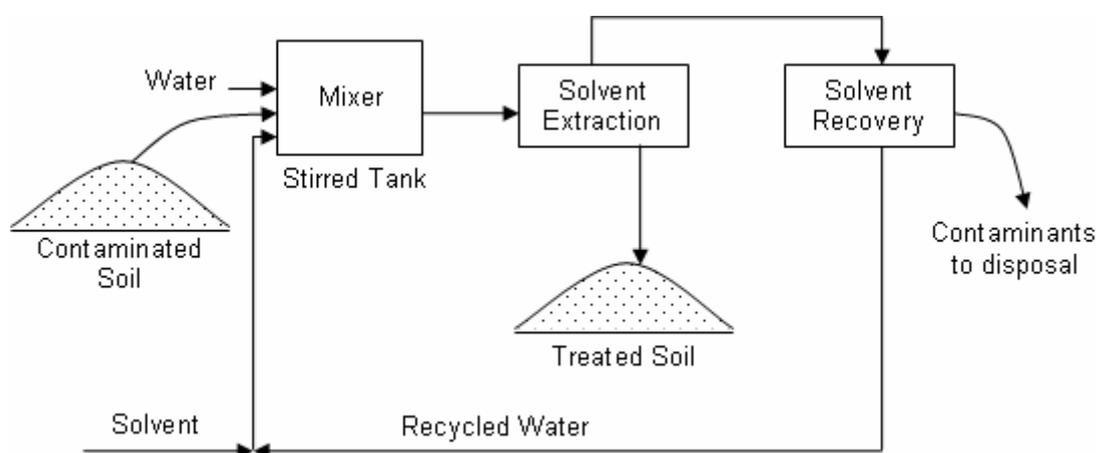
Fig. 12. Solvent extraction process

The method is applicable for process equipment requiring decontamination for reuse. It is also applicable for explosive items, such as mines and shells, being demilitarized (after removal of explosives) or scrap material contaminated with explosives.

The method can also be used for buildings or structures associated with ammunition plants, arsenals, and depots involved in the manufacture, processing, loading, and storage of pyrotechnics, explosives, and propellants.

The following factors may limit the applicability and effectiveness of the process:
- the costs of this method are higher than open burning.
- flash chamber design must take into consideration possible explosions from improperly demilitarized mines or shells.
- the rate at which equipment or material can be decontaminated is slower than that for open burning.

4.2. Incineration

High temperatures, 870 to 1.200ºC, are used to volatilize and combust (in the presence of oxygen) halogenated and other refractory organics in hazardous wastes. The destruction and removal efficiency (DRE) for properly operated incinerators exceeds the 99.99% requirement for hazardous waste and can be operated to meet the 99.9999% requirement for PCBs and dioxins (EPA, 1987).

Commercial incinerator designs are rotary kilns, equipped with an afterburner, a quench, and an air pollution control system, Figure 14. The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber and operates at temperatures up to 980ºC. An experimental unit, the circulating fluidized bed (CFB), uses high-velocity air to circulate and suspend the waste particles in a combustion loop and operates at temperatures up to 870ºC. Another experimental unit, the infrared unit uses electrical resistance heating elements or indirect – fired radiant U-tubes to heat material passing through the chamber on a conveyor belt and operates at temperatures up to 870ºC (Soesilo and Wilson 1997).

Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NO_x, and SO_x). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. Limestone or caustic solution added to the combustor loop removes acid gases in the CFB.
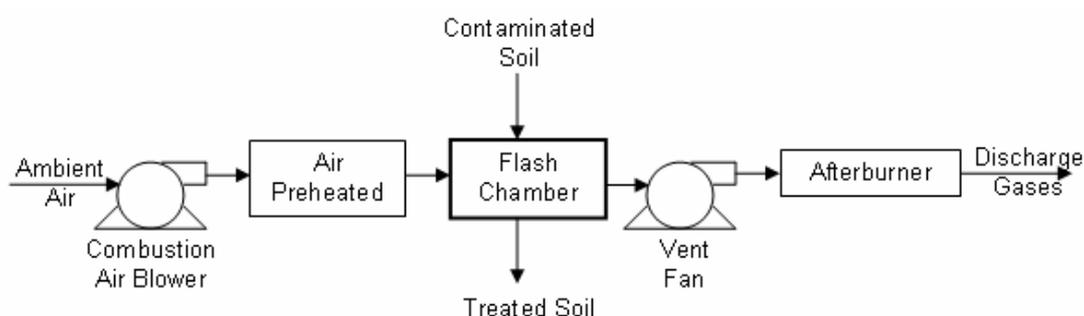
Fig. 13. Hot gas decontamination
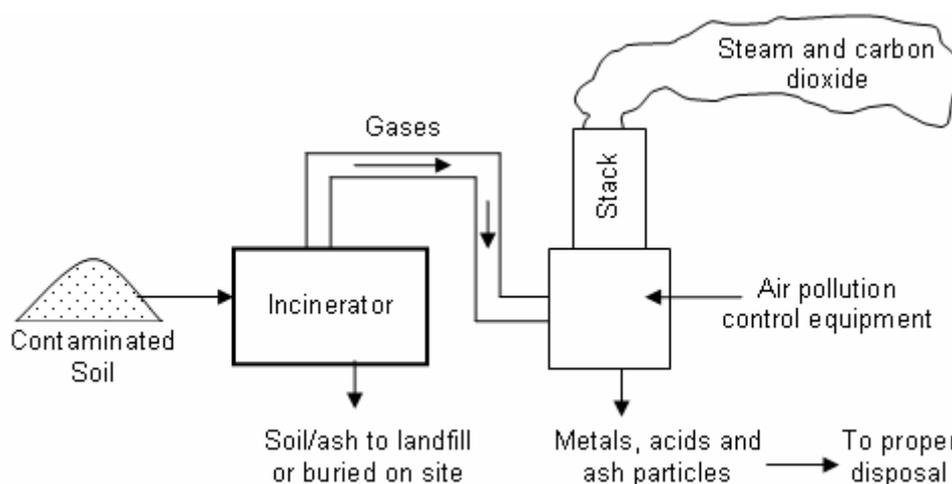
Fig. 14. Incineration process

Incineration is used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs, and dioxins. Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- only one off-site incinerator is permitted to burn pcbs and dioxins.
- there are specific feed size and materials handling requirements that can impact applicability or cost at specific sites.
- heavy metals can produce a bottom ash that requires stabilization.
- volatile heavy metals, including lead, cadmium, mercury, and arsenic, leave the combustion unit with the flue gases and require the installation of gas cleaning systems for removal.
- metals can react with other elements in the feed stream, such as chlorine or sulfur, forming more volatile and toxic compounds than the original species. such compounds are likely to be short – lived reaction intermediates that can be destroyed in a caustic quench.
- sodium and potassium form low melting point ashes that can attack the brick lining and form a sticky particulate that fouls gas ducts.

If an off-site incinerator is used, the potential risk of transporting the hazardous waste through the community must be considered.

4.3. Open burn (OB) and open detonation (OD)

Open burn (OB) and open detonation (OD), operations are conducted to destroy unserviceable, unstable, or unusable munitions and explosives materials. In OB operations, explosives or munitions are destroyed by selfsustained combustion, which is ignited by an external source, such as flame, heat, or a detonation wave (that does not result in a detonation). In OD operations, Fig. 15, detonatable explosives and munitions are destroyed by a detonation, which is initiated by the detonation of a disposal charge (Teer et al., 1993).

OB/OD operations can destroy many types of explosives, pyrotechnics, and propellants. OB areas must be able to withstand accidental detonation of any or all explosives being destroyed, unless the operating OB technicians recognize that the characteristics of the materials involved are such that orderly burning without detonation can be ensured. Personnel with this type of knowledge must be consulted before any attempt is made at OB disposal, especially if primary explosives are present in any quantity.

OB and OD can be initiated either by electric or burning ignition systems. In general, electric systems are preferable because they provide better control over the timing of the initiation. In an electric system, electric current heats a bridge wire, which ignites a primary explosive or pyrotechnic, which, in turn, ignites or detonates the material slated to be burned or detonated. If necessary, safety fuses, which

consist of propellants wrapped in plastic weather stripping, are used to initiate the burn or detonation (USAMC, 1985).
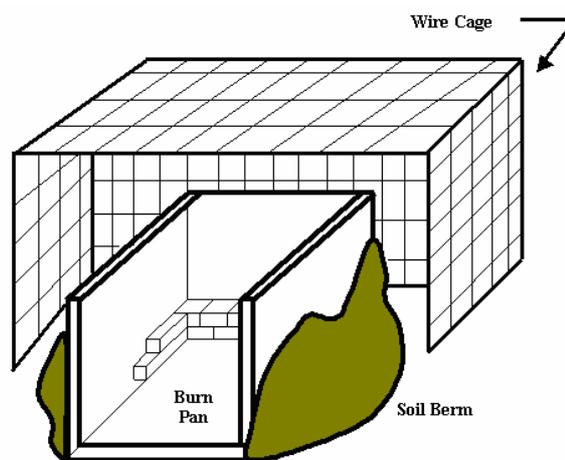
Fig. 15. Open burn (OB) and open detonation (OD)

OB/OD can be used to destroy unserviceable, unstable, or unusable munitions and explosive materials. The applicability and effectiveness of the process could be limited by:

- minimum distance requirements for safety purposes mean substantial space is required.
- ob/od operations emissions are difficult to capture for treatment and may not be permitted in areas with emissions limitations.
- ob/od operations require that prevailing winds carry sparks, flame, smoke, and toxic fumes away from neighboring facilities. ob/od operations are never conducted during sand, snow, or electrical storms strong enough to produce static electricity, which might cause premature detonation.
- in addition, with growing ob/od restriction, dod's ability to treat energetic wastes is diminishing and energetic disposal may be eliminated.

4.4. Pyrolysis

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen (Soesilo and Wilson 1997). Because some oxygen will be present in any pyrolytic system, nominal oxidation will occur. If volatile or semivolatile materials are present in the waste, thermal desorption will also occur, Fig. 16.

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

hydrocarbons. If the offgases are cooled, liquids condense producing an oil/tar residue and contaminated water. Pyrolysis typically occurs under pressure and at operating temperatures above 430ºC. The pyrolysis gases require further treatment. The off-gases may be treated in a secondary combustion chamber, flared, and partially condensed. Particulate removal equipment such as fabric filters or wet scrubbers are also required.

Pyrolysis is an emerging technology. Although the basic concepts of the process have been validated, the performance data for an emerging technology have not been evaluated according to methods approved by EPA and adhering to EPA quality assurance/quality control standards (EPA, 1992).

The target contaminant groups for pyrolysis are SVOCs and pesticides. The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint waste. Pyrolysis systems may be applicable to a number or organic materials that "crack" or undergo a chemical decomposition in the presence of heat.

Pyrolysis has shown promise in treating organic contaminants in soils and oily sludges. Chemical contaminants for which treatment data exist include PCBs, dioxins, PAHs, and many other organics. Pyrolysis is not effective in either destroying or physically separating inorganics from the contaminated medium. Volatile metals may be removed as a result of the higher temperatures associated with the process but are similarly not destroyed.

The limitative factors for the applicability and effectiveness of the process include (FRTR, 2000):
- there are specific feed size and materials handling requirements that impact applicability or cost at specific sites.

- the technology requires drying of the soil to achieve a low soil moisture content (<1%).
- highly abrasive feed can potentially damage the processor unit.
- high moisture content increases treatment costs.
- treated media containing heavy metals may require stabilization.

4.5.1. High temperature thermal desorption (HTTD)

High temperature thermal desorption (HTTD) is a full – scale technology (Fig. 17), in which wastes are heated to 560ºC to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system. HTTD systems are physical separation processes and are not designed to destroy organics. Bed temperatures and typical residence times will cause selected contaminants to volatilize but not be oxidized (Anderson, 1993).

HTTD is frequently used in combination with incineration, solidification/stabilization, or dechlorination, depending upon site – specific conditions. The technology has proven it can produce a final contaminant concentration level below 5 mg/kg for the target contaminants identified (Khan et al., 2004).

The target contaminants are SVOCs, PAHs, PCBs, and pesticides; however, HTTD systems have varying degrees of effectiveness against the full spectrum of organic contaminants. VOCs and fuels also may be treated, but treatment may be less cost - effective. Volatile metals may be removed by HTTD systems. The presence of chlorine can affect the volatilization of some metals, such as lead. The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote – contaminated soils, hydrocarbon-contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint wastes.
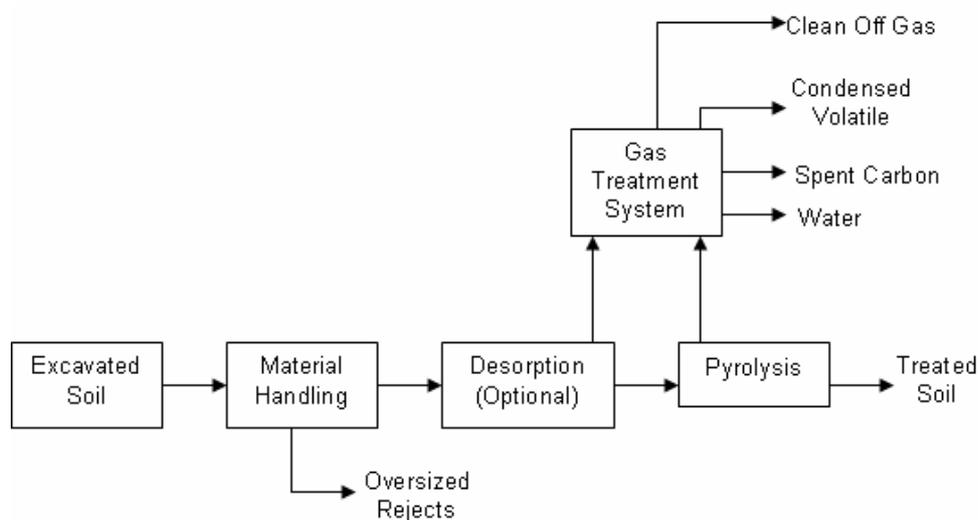
Fig. 16. Pyrolysis

The applicability and effectiveness of the process include could be limited by the following factors (FRTR, 2000; Johnson et al., 1987):

- feed particle size greater than 2 inches can impact applicability or cost at specific sites.
- dewatering may be necessary to reduce the amount of energy required to heat the soil.
- highly abrasive feed can potentially damage the processor unit.
- clay and silty soils and high humic content soils increase reaction time as a result of binding of contaminants

4.5.2. Low temperature thermal desorption (LTTD)

Low temperature thermal desorption (LTTD) systems are physical separation processes and are not designed to destroy organics. Wastes are heated to between 90 and 320ºC to volatilize water and organic contaminants, Fig. 18. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system.

The bed temperatures and residence times designed into these systems will volatilize selected contaminants but will typically not oxidize them. LTTD is a full-scale technology that has been proven successful for remediating petroleum hydrocarbon contamination in all types of soil.

Contaminant destruction efficiencies in the afterburners of these units are greater than 95%. The same equipment could probably meet stricter requirements with minor modifications, if necessary. Decontaminated soil retains its physical properties and ability to support biological activity (Lighty et al., 1987).

Two common thermal desorption designs are the rotary dryer and thermal screw. Rotary dryers are horizontal cylinders that can be indirect - or direct fired.

The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot oil or steam circulates through the auger to indirectly heat the medium.
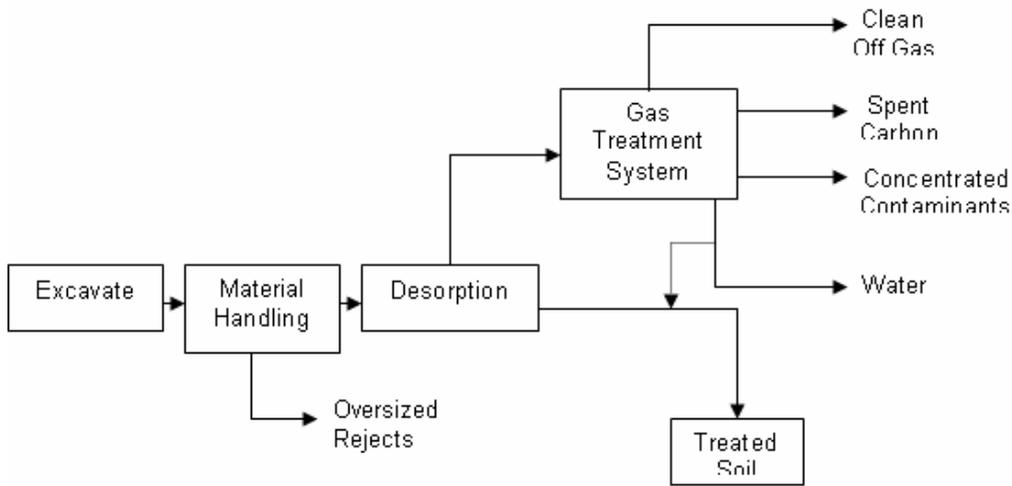
Fig. 17. High temperature thermal desorption (HTTD)
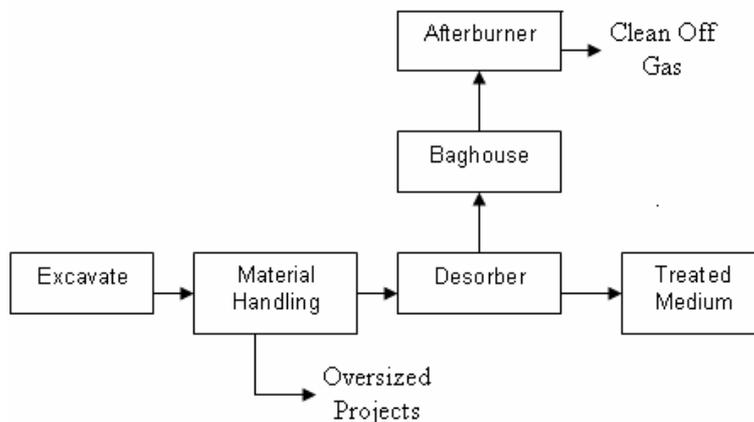
Fig. 18. Low temperature thermal desorption

All thermal desorption systems require treatment of the off-gas to remove particulates and contaminants. Particulates are removed by conventional particulate removal equipment, such as wet scrubbers or fabric filters. Contaminants are removed through condensation followed by carbon adsorption, or they are destroyed in a secondary combustion chamber or a catalytic oxidizer. Most of these units are transportable (EPA, 1994).

The target contaminant groups for LTTD systems are nonhalogenated VOCs and fuels. The technology can be used to treat SVOCs at reduced effectiveness. Factors that may limit the applicability and effectiveness of the process include:

- there are specific feed size and materials handling requirements that can impact applicability or cost at specific sites.
- dewatering may be necessary to achieve acceptable soil moisture content levels.
- highly abrasive feed potentially can damage the processor unit.
- heavy metals in the feed may produce a treated solid residue that requires stabilization.

All *ex-situ* soil thermal treatment systems employ similar feed systems consisting of a screening device to separate and remove materials greater than 5 centimeters, a belt conveyor to move the screened soil from the screen to the first thermal treatment chamber, and a weight belt to measure soil mass. Occasionally, augers are used rather than belt conveyors, but either type of system requires daily maintenance and is subject to failures that shut the system down. Soil conveyors in large systems seem more prone to failure than those in smaller systems. Size reduction equipment can be incorporated into the feed system, but its installation is usually avoided to minimize shutdown as a result of equipment failure.

Soil storage piles and feed equipment are generally covered as protection from rain to minimize soil moisture content and material handling problems. Soils and sediments with water contents greater than 20 to 25% may require the installation of a dryer in the feed system to reduce the energy cost to heat the soil.

Some volatilization of contaminants occurs in the dryer, and the gases are routed to a thermal treatment chamber.

4.6. Ex-situ vitrification

Ex-situ vitrification is designed to encapsulate inorganic contaminants, rather than reduce contaminant concentrations. Destruction of the organic contaminants present in the treated media, however, does occur because of temperatures achieved in the process (Fig. 19)(DOE, 1993).

Ex-situ vitrification is effective in reducing the mobility of the contaminated wastes within the media. The vitrified mass has high strength and resistance to leaching. The strength properties of material vitrified by different systems can vary widely. Systems in which the vitrified mass is quench-cooled may produce a more easily fractured mass than systems in which the mass is allowed to air cool. Systems in which fluxing agents are used will also have different strength properties. The composition of the soil that is vitrified may also affect the strength properties of the vitrified material.

Ex-situ vitrification is normally considered a standalone technology; however, its potential for use in treating the solid residuals from other technologies, such as incinerator ash, is receiving increasing attention (Circeo, 1991).

Ex-situ vitrification is applicable to the full range of contaminant groups, but inorganics is the target contaminant group. Metals, radionuclides, etc. are encapsulated in the vitrified mass, resisting leaching for geologic time periods.

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- organic off-gases need to be controlled. some volatile heavy metal and radioactive contaminants may volatilize and require treatment in the off-gas system.
- use or disposal of the resultant vitrified slag is required.
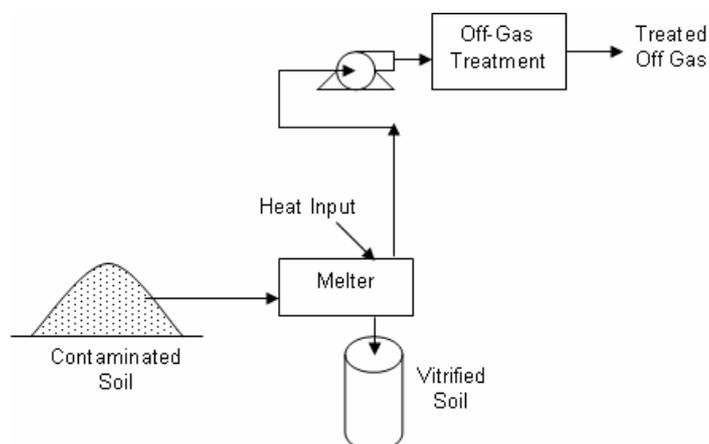
Fig. 19. *Ex- situ* vitrification

5. Excavation, retrieval, and off-site disposal

Contaminated material is removed and transported to permitted off-site treatment and/or disposal facilities. Some pretreatment of the contaminated media usually is required in order to meet land disposal restrictions (Church, 1981).

Excavation and off-site disposal is applicable to the complete range of contaminant groups with no particular target group. Although excavation and off-site disposal alleviates the contaminant problem at the site, it does not treat the contaminants.

Limiting factors that may limit the applicability and effectiveness of the process include:
- generation of fugitive emissions may be a problem during operations.
- the distance from the contaminated site to the nearest disposal facility will affect cost.
- depth and composition of the media requiring excavation must be considered.
- transportation of the soil through populated areas may affect community acceptability.
- disposal options for certain waste (e.g., mixed waste or transuranic waste) may be limited (EPA, 1991).

6. Conclusions

The main advantage of ex situ treatment is that it generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. However, ex situ treatment requires excavation of soils, leading to increased costs and engineering for equipment, possible permitting, and material handling/worker exposure considerations.

Bioremediation techniques are destruction or transformation techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favorable environmental for the microorganisms. Generally, this means providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH. Sometimes, microorganisms adapted for degradation of the specific contaminants are applied to enhance the process.

Biological processes are typically easily implemented at low cost. Contaminants can be destroyed or transformed, and little to no residual treatment is required; however, the process requires more time and difficult to determine whether contaminants have been destroyed. Biological treatment of PAHs leaves less degradable PAHs (cPAHs) behind. These higher molecular cPAHs are classified as carcinogens. Also, an increase in chlorine concentration leads to a decrease in biodegradability. Some compounds, however, may be broken down into more toxic by-products during the bioremediation process.

An advantage over the in situ applications is that in ex situ applications, these byproducts are contained in the treatment unit until nonhazardous end-products are produced. Although not all organic compounds are amenable to biodegradation, bioremediation techniques have been successfully used to remediate soils, sludges, and groundwater contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals. Bioremediation is not generally applicable for treatment of inorganic contaminants.

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy, separate, or contain the contamination. Chemical reduction/oxidation and dehalogenation (BCD or glycolate) are destruction technologies. Soil washing, SVE, and solvent extraction are separation techniques, and stabilization/solidification is an immobilization technique.

Physical/chemical treatment is typically cost effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is not engineering or energy-intensive. Treatment residuals from separation techniques will require treatment or disposal, which will add to the total project costs and may require permits.

Thermal treatments offer quick cleanup times but are typically the most costly treatment group. This difference, however, is less in ex situ applications than in in situ applications.

Thermal processes use heat to increase the volatility (separation); burn, decompose, or detonate (destruction); or melt (immobilization) the contaminants.

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