Petroleum Contaminated Soils Remediation Technologies

Environmental Issues | Petroleum Contaminated Soils Remediation Technologies

[ww-shortcode-divider]

1.Introduction

Petroleum is one of the most important energy resources and a raw material of the chemical industry. Nevertheless oil spills during exploration, transportation, and refining, can cause some environmental problems to soil, groundwater and air.

There are various remediation techniques available for environmental restoration activities and can be classified in several ways such as in situ or ex situ, those for soil , surface or groundwater remediation, or basing on the physics or chemistry of the treatment.

The majority of techniques are categorized as physical treatments with only one process, biodegradation, falling under the biological treatment category. Chemical treatments involve the application of agents to promote extraction of the hazardous substance, and physical treatments involve removal of the hazard through physical means. The relative benefit of the various remediation methods has dependence in large-scale applicability as well as overall cost.

2. Current Technologies

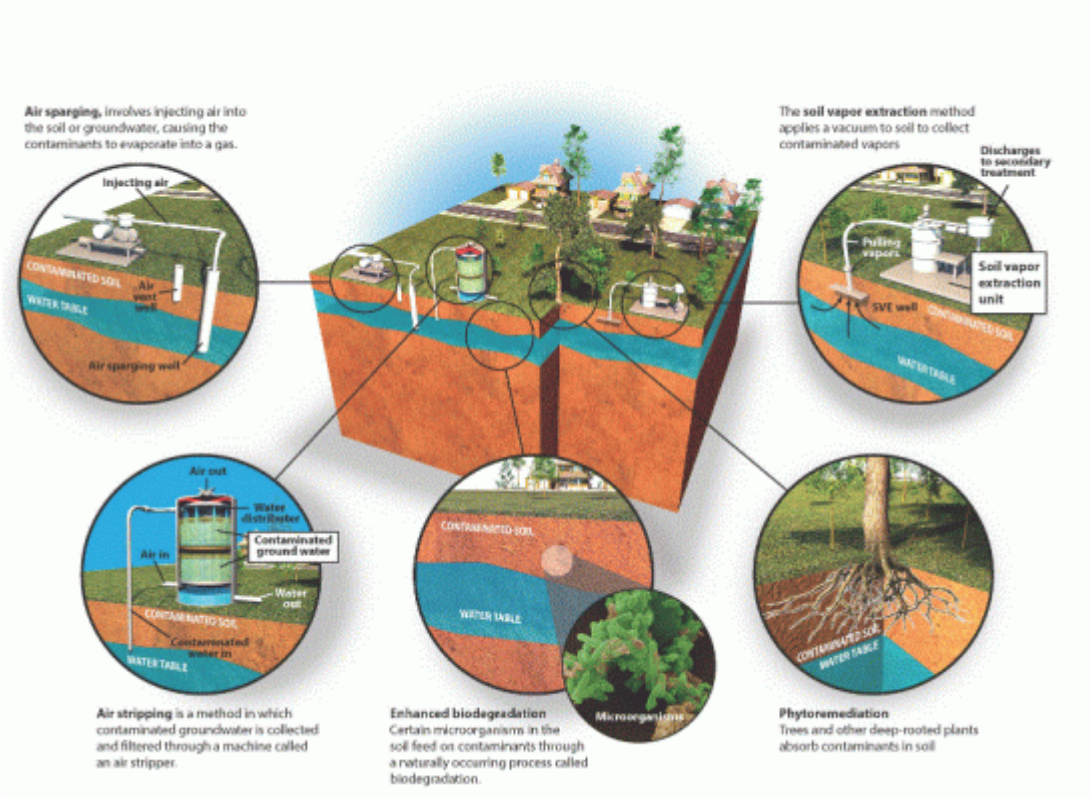


Fig. 1 Remediation methods

Three primary strategies used separately or in conjunction to remediate most sites are:

- Elimination or alteration of contaminants.
- Extraction or separation of contaminants from environmental media.
- Immobilization of contaminants.

Treatment technologies capable of contaminant elimination by altering their chemical/physical structure are:

- thermal
- biological
- chemical

These elimination technologies can be applied in situ or ex situ to contaminated media.

Treatment technologies commonly used for extraction and separation of contaminants from environmental media include

• soil treatment by thermal desorption • soil washing • solvent extraction • oil vapor extraction (SVE)	• ground water treatment by either phase separation • carbon adsorption • air stripping • ion exchange

or some combination of these technologies.

Immobilization technologies include stabilization, solidification, and containment technologies, such as placement in a secure landfill or construction of slurry walls. No immobilization technology is permanently effective, so some type of maintenance is desired. Stabilization technologies are often proposed for remediating sites contaminated by metals or other inorganic species.

Selection and integration of technologies should use the most effective contaminant transport mechanisms to arrive at the most effective treatment scheme. For example, more air than water can be moved through soil. Therefore, for a volatile contaminant in soil that is relatively insoluble in water, SVE would be a more efficient separation technology than soil flushing or washing.

These concepts about site remediation strategies and representative technologies associated with them are summarized in Figure 2.[1]

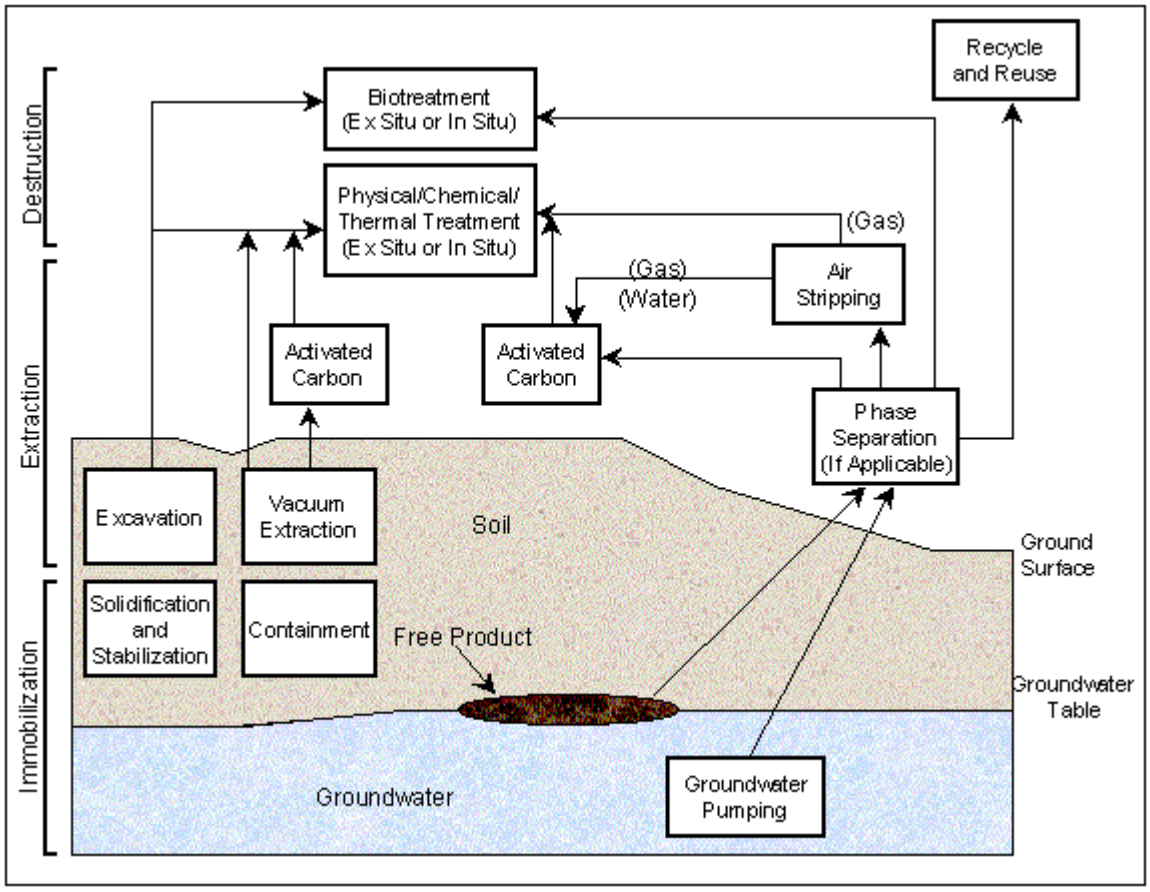


Fig. 2 Classification of remedial technologies by function

Generally, no single technology can remediate an entire site. Several treatment technologies are usually combined at a single site to form what is known as a treatment train.

Remediation of Soils

Used and abandoned sites contain soils contaminated by petroleum hydrocarbons. These would have resulted from spills and leaks of gasoline, kerosene, fuels, diesels, lubricating oils and similar products during the years of industrial activities at the site. Some soils at old sites also get contaminated by PCB, and metals such as Zinc, lead, cadmium.

Excavation and Disposal ("Dig and Dump")

Earlier practices of excavation and disposal involved digging

out contaminated soil from the location of contamination and dumping it off in a landfill or other locations (e.g. a depression) where the contaminated soil is not considered a hazard to human and ecological health. No treatment might have been carried out on the contaminated soil prior to dumping at the target site; hence the approach is nick-named “Dig and Dump”. Regulatory restrictions on land disposals have brought some changes to this practice. In North America and most countries in Europe, it is now illegal to co-dispose hazardous and non-hazardous wastes in landfills. There are only designated or licensed landfill sites that accept PHC contaminated soils. Furthermore, disposal in landfill sites without pre-treatment is now outlawed in several jurisdictions. Wastes for disposal in landfills should be characterized and the parameters must meet certain pre-specified waste acceptance criteria. Dig and Dump approach is very simple to implement. However, its main disadvantages are cost of transporting the contaminated soil to its final destination and the contamination (if soil is dumped untreated) of the final destination (in case of future re-use).

Chemical Treatments

Oxidation, in waste remediation, refers to the movement of a contaminant to a more oxidized or more environmentally benign state. It involves the use of chemicals for the destruction of organic contaminant constituents. The chemical oxidants most commonly employed to date include peroxide, ozone, chlorine dioxide and permanganate. They can oxidize hazardous materials that are either organic or inorganic compounds.

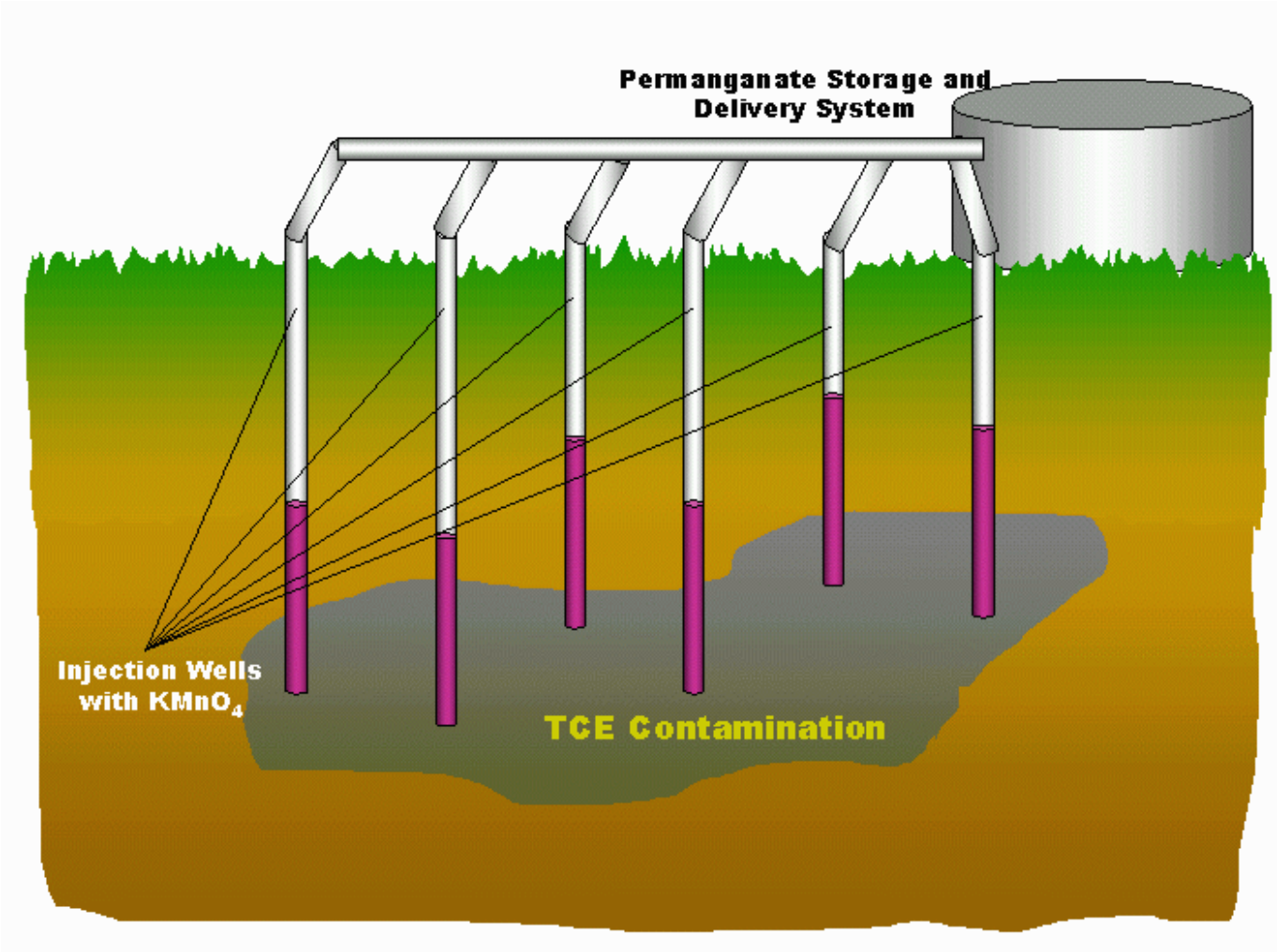


Fig. 3 Oxidation Treatment

Depending on site and contamination characteristics, in situ chemical treatment can be achieved by either injection of liquid, gaseous, and colloidal reactive chemicals into subsurface soils and/or aquifers, or by installation of a permeable chemical treatment wall across the ground-water flow path.

The successful application of a particular in situ chemical treatment technique requires

- effective chemical reaction of the introduced chemical with contaminants at a proper rate and extent
- effective delivery of the reagents throughout the zone

to be treated.

A primary obstacle for in situ chemical treatment techniques involves delivery, distribution and mass transfer of chemicals in subsurface environments. A major concern for in situ chemical flushing is the uncertainty of the fate and effects of washing reagents in the subsurface environment.[2]

The table below provides some features for application of oxidation for in situ treatment.

Site-specific information is needed for field application.

Technology	**Chemical Injection – Oxidation**		
Materials	**Hydrogen Peroxide**	**Permanganate**	**Ozone**
Treatable Compounds	Chlorinated solvents, polyaromatic hydrocarbons, and petroleum products. Not effective for chlorinated alkanes and saturated aliphatic hydrocarbons.		
Influencing Factors			
pH	Prefer low pH of 2 to 4, but feasible up to near neutral pH	Prefer neutral pH of 7 to 8, but effective over a wide range.	Effective at natural soil pH
Permeability	Prefer high permeability, but feasible for low permeability with use of advanced oxidant delivery techniques, such as deep soil mixing and soil fracturing. Fenton's reagent and ozone rely on free radical generation and thus transport away from point of injection is constrained.		
Temperature	All oxidants are affected by temperature to varying degrees.		
Depth	With use of the advanced delivery techniques, depth is generally not a limitation.		
Oxidant Degradation	Easily degraded in contact with soil/groundwater.	The oxidant is very stable	Ozone degradation in soils is limited.

Other factors	May need to supply iron ($FeSO_4$) to form Fentonís reagent.		
Potential Detrimental Effects	Particulates can be generated and permeability loss is possible. Potential side effects include gas evolution with peroxide and ozone and generation of fugitive emissions, potentially toxic byproducts, potential effects on/of metals and reduction of biomass.		

Tab. 1 Summary of In Situ Chemical Treatment Technologies by Chemical Injection of Oxidants

Another chemical method is the chemical extraction. It 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. They vary in regard to the chemical employed, type of equipment used, and mode of operation. There are:

- Acid Extraction: uses hydrochloric acid to extract heavy metal contaminants from soils.
- Solvent extraction: uses organic solvent as the extractant. It is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing, depending upon site-specific conditions. Acid extraction is suitable to treat sediments, sludges, and soils contaminated by heavy metals. 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 waste.

Factors that may limit the applicability and effectiveness of the process include:

- Some soil types and moisture content levels will

adversely impact process performance.

- Higher clay content may reduce extraction efficiency and require longer contact times.
- 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.
- After acid extraction, any residual acid in treated soil needs to be neutralized.
- Capital costs can be relatively high and the technology may be more economical at larger sites.

Physical Treatments

Several physical treatments are available for soil remediation.

Capping

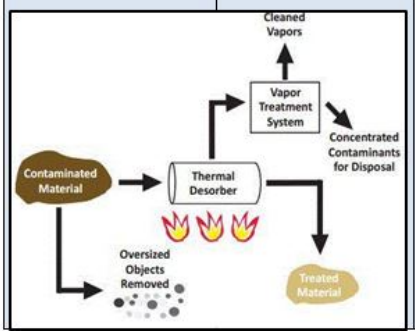
Cover systems provide a stabilization mechanism by reducing the amount of water through-put in a burial trench or retention basin. The cover typically is composed of a surface layer that supports vegetation, a drainage layer, a low-permeability layer, and a gas-venting layer. The requirements of the site dictate which layers are necessary, and some sites will not need all layers. The decomposition of organic matter results in the generation of methane gas. If uncontrolled, gas that migrates within the cover system can balloon and possibly combust.

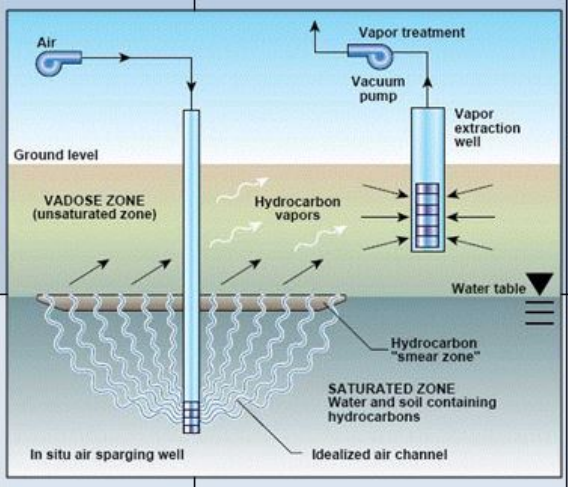
Cementitious Waste Forms

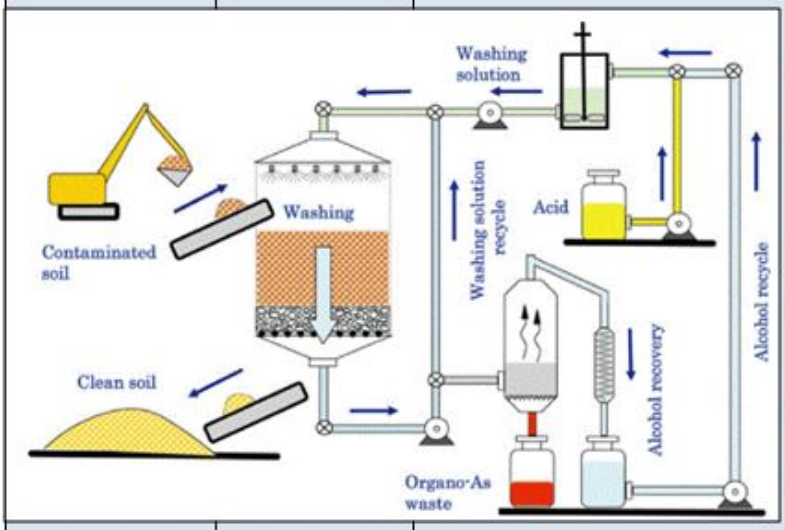
Sulfur polymer cement (SPC) has been used to stabilize high loadings of volatilized toxic metals. SPC is a sulfur composite material with a melting point of 110-120 °C,that resists attack by most acids and salts. The advantages of SPC are:

- it has a greater waste-to-agent ratio than concrete;
- it has the ability to be remelted and reformed;
- it is less permeable than concrete;
- in its final waste form it is devoid of water;
- it can be processed at relatively low temperatures

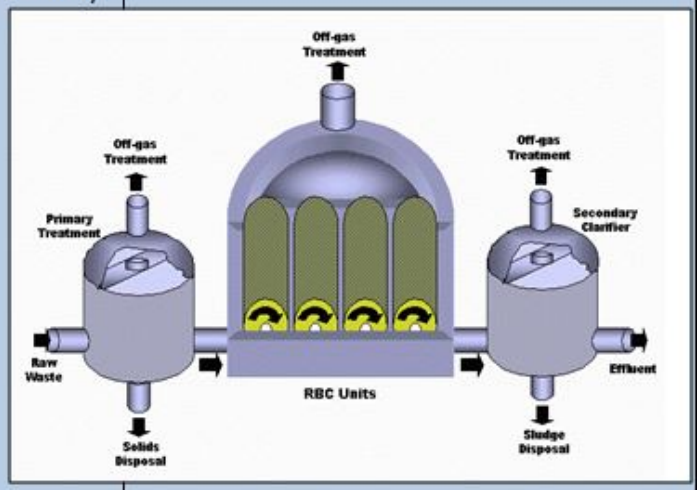
Others methods which require more technological processes and installations are summarized in the table below with their advantages and disadvantages.

SOIL Physical Treatments	Applicability	PROS	COS
Incineration Technologies There are several types of incinerators: • rotary kiln, • infrared furnaces, • liquid injection, • plasma arc, • fluidized bed	Ex Situ	• efficiently destroy chemical contaminants • reduce the toxicity and volume of substances at hazardous waste sites.	• Off gases and combustion residuals generally require treatment • The toxicity of radioactive contaminants would not be eliminated • the waste's matrix influences the technical complications and the economics of incineration • Heavy metals can produce a bottom ash that requires stabilization.
Thermal Desorption 	Ex Situ	• reduced amount of gases produced • reducing the size of the off-gas handling system	• There are specific particle 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.

SOIL Physical Treatments	Applicability	PROS	COS
<u>Soil Vapour Extraction (SVE)</u> SVE pull vapors out, from soil above the water table by application of vacuum.	In Situ  	• Is effective for use in the upper soil layer or the unsaturated/vadoze soil zone.	• Soil that has a high percentage of fines and a high degree of saturation will require higher vacuums (increasing costs) • Large screened intervals are required in extraction wells for soil with highly variable permeabilities or stratification • Soil that has high organic content or is extremely dry has a high sorption capacity of VOCs, which results in reduced removal rates. • Exhaust air and off-gas from in situ SVE system may require treatment to eliminate possible harm to the public and the environment.
<u>Air Sparging</u> Air is pumped to push contaminants from groundwater and wet soil from beneath the water table.	In Situ	• Removes lighter molecule PHC constituents such as benzene, ethylbenzene, toluene, and xylene (BTEX), from petroleum products like gasoline from the saturated soil zone	• Air flow through the saturated zone may not be uniform, which implies that there can be uncontrolled movement of potentially dangerous vapors. • Depth of contaminants and specific site geology must be considered. • Air injection wells must be designed for site-specific conditions. • Soil heterogeneity may cause some zones to be relatively unaffected.

SOIL Physical Treatments	Applicability	PROS	COS
<u>Soil Washing</u> Contaminants sorbed onto fine soil particles are separated from bulk soil in a water-based system on the basis of particle size. The wash water may be augmented with a basic leaching agent, surfactant, or chelating agent	Ex Situ	• provides a cost effective and environmentally proactive alternative to stabilization and land filling. • offers the ability for recovery of metals • can clean a wide range of organic and inorganic contaminants from coarse-grained soils.	• 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 at demobilization. • Additional treatment steps may be required to address hazardous levels of washing solvent remaining in the treated residuals. • It may be difficult to remove organics adsorbed onto clay-size particles.
	In Situ		• Depth of contaminants may limit some types of application processes. • Future usage of the site may "weather" the materials and affect ability to maintain immobilization of contaminants. • Some processes result in a significant increase in volume (up to double the original volume). • Certain wastes are incompatible with variations of this process. Treatability studies are generally required. • Reagent delivery and effective mixing are more difficult than for ex situ applications. • Like all in situ treatments, confirmatory sampling can be more difficult than for ex situ treatments. • The solidified material may hinder future site use. • Processing of contamination below the water table may require dewatering.
			

SOIL Physical Treatments	Applicability	PROS	COS
Biological Treatments Biodegradation generally refers to the breakdown of organic compounds by living organisms. Inorganic compounds can be transformed into compounds having more or less mobility or toxicity than their original. Air emissions from the "biopile" are treated by biofiltration where the pollutants are degraded and mineralized by heterotrophic aerobic microorganisms.	In Situ	• allows soil to be treated without being excavated and transported • can be used to change the valence state of inorganics and cause adsorption, immobilization onto soil particulates, precipitation, uptake, accumulation, and concentration of inorganics in micro or macroorganism • generally, petroleum hydrocarbons can be readily bioremediated, at relatively low cost	• low land requirement • low capital and operating costs • good process control • the potential of hydrocarbon biodegradation depends on the availability of desired microorganisms.



Tab. 2 Remediation Methods

Water Treatments

Water is by far the largest byproduct of the fossil fuel industry, thus a special effort requires the water treatment. Early treatment remedies for groundwater contamination were primarily pump-and-treat operations. This method involves extracting contaminated groundwater via wells or trenches and treating the groundwater above ground (ex situ) using processes such as air stripping, carbon adsorption, biological reactors, or chemical precipitation. Many of these processes produce highly contaminated wastes that then have to be

disposed.

Some of the techniques for ground and surface water are summarized in the table below.[3]

WATER Remediation Techniques	Degree of Effectiveness	Cost	Technological Development/ Research Needs
Biological Treatments			
	• Specific environment governs success of process • Aerobic fluidized-bed had high chlorophenol loading rates	• Technique is expensive • Heating of water is a prerequisite which radically increases costs	• Little experience with in-situ bioremediation of groundwater • Little is known about fungal adaptation and processes in degradation of anthropogenic substances
Chemical Treatments			
Electron-Beam Irradiation	• Low dose rates of electrons more efficient • E-beam technology has shown removal efficiencies up to 99.99% in full-scale operation		• Promising technology • Shown to be effective and economical for removal or hazardous organic compounds through lab and pilot plant studies
Radiocolloid Treatment	• In-situ colloid remediation process using polyelectrolyte capture successful in laboratory column tests		Further work necessary to demonstrate at actual site
Removal by Sorption to Organo-Oxides	• Can be regenerated in-situ • Selective removal achieved if specific surfactant that sorbs contaminant selectively is used • Solute removed can be recovered		Batch and column experiments done to demonstrate use of organo -oxide for treatment of nonionic organic pollutants

Physical Treatments			
Air Sparging/ Air Stripping In-Situ Air Sparging (IAS) Pump & Treat (P&T)	• Efficiency with which O_2 is transferred to groundwater must be addressed if IAS to be proven effective • Air and steam stripping technologies most effective with VOCs and ammonia	In-well aeration (IAS) has potential to be more cost-effective and efficient than conventional P&T	• Much to be learned about in-well aeration • Because of potential for loss of control, air sparging systems should never by installed without a pilot test

Tab. 3 Water Remediation Techniques

3.Research & Development

Others remediation techniques summarized in this part are still in the investigational stages, have been applied only in the laboratory or on a small scale or in few projects..

Remediation Using Actinide Chelators

Research groups are working to design and synthesize organic chelators for selective binding of actinide ions from soils and waste streams. Their studies show that multidentate oxoligands such as hydroxamate, iminodiacetate, and hydroxypyridinones are potential candidates for binding actinide ions present in acidic, aqueous solutions. They have also identified and synthesized chelating agents for plutonium. Specific application under the complex conditions relevant to environmental remediation strategies for actinides is in an early stage of development. Potential solubility problems, stability, and pH requirements exist that could limit the use of chelators. [4]

Critical Fluid Extraction

Organic compounds, primarily PCBs and PAHs, appear to be the most amenable to extraction from soils and sludges with a technique utilizing liquefied gas, typically carbon dioxide, propane, butane, and sometimes alcohol. High pressure and moderate temperatures are used to compress the gas to fluid state. At the critical temperature and pressure, where the fluid state occurs, the mass transfer capabilities of the "critical fluid" are at their best. Volatile and semivolatile organics in liquid and semi-solid wastes have been removed with 99.9 percent efficiencies in the laboratory.

Photolysis

Many organic compounds absorb light energy at visible or ultraviolet wavelengths. This energy promotes the decomposition of the chemical. Ultraviolet radiation is sufficient to cleave many types of covalent bonds. It has been shown to degrade PCBs, dioxins, PAHs, and several aromatic constituents of gasoline, including benzene, toluene, ethylbenzene, and xylene. Liquid, gaseous, and solid media are suitable to such treatment. Ultraviolet light is sometimes used to intensify the oxidation process in the presence of the principal oxidizing chemicals, such as ozone or hydrogen peroxide.

Electrokinetic Oxidation

Oxidation of soil using low voltage pulsed current to achieve electrokinetic and Electrochemical Redox reactions. The EKOGRID™ technology utilizes low voltage DC power source and optimized pulsed voltage patterns distributed to steel rod electrodes that are installed around and in the area to be treated, referred to as "The Grid." Installed electrodes should reach the depth of polluted soil or ground water.

Description of Process and Scientific Principles

The technology works best in capillary soil conditions, in which the effective oxidizing agents (i.e. radicals and oxygen) are formed at the surface of each grain of soil and evenly spread. The finer the soil grain size, the more effectively the system operates (faster and more complete remediation). Electrokinetic oxidation systems based on electrodes and low voltage control unit can be installed on dry land or underwater to treat bottom sediments. It also works in fractured porous bed rock. The system utilizes the soil matrix and reactions that occur at the surface of each grain, precisely where the pollution is.

Electrokinetic oxidation utilizes reaction products in electrochemical and electro kinetic processes to oxidize organic pollutants in humid porous matrices. In these reactions, free radicals and oxygen are generated which enhance the remediation process. Electrokinetic oxidation is a remediation method that provides enhanced bioremediation; microbiological activity is boosted with oxygen formed in the reactions. The EKOGRID patented pulsing voltage output creates redox reactions (e.g. electrolysis) on the pore surfaces and the electro-osmotic forces move the charged contents of the pore water quickly back and forwards. Freshly formed oxygen and hydroxyl radicals will oxidise and split hydrocarbon chains to lighter fractions, finally forming carbon dioxide and water, which are the final end products. The formation of oxygen will activate the microbes able to decompose various types of organic contaminants. As a result EKOGRID™ is not only a technology to crack hydrocarbons, but also an enhanced bioremediation method. Optimizing the environmental conditions for the microorganisms, for example the availability of nutrients, and follow-up of the microbe activity, for example through soil respiration, is an important part of the EKOGRID™ process.

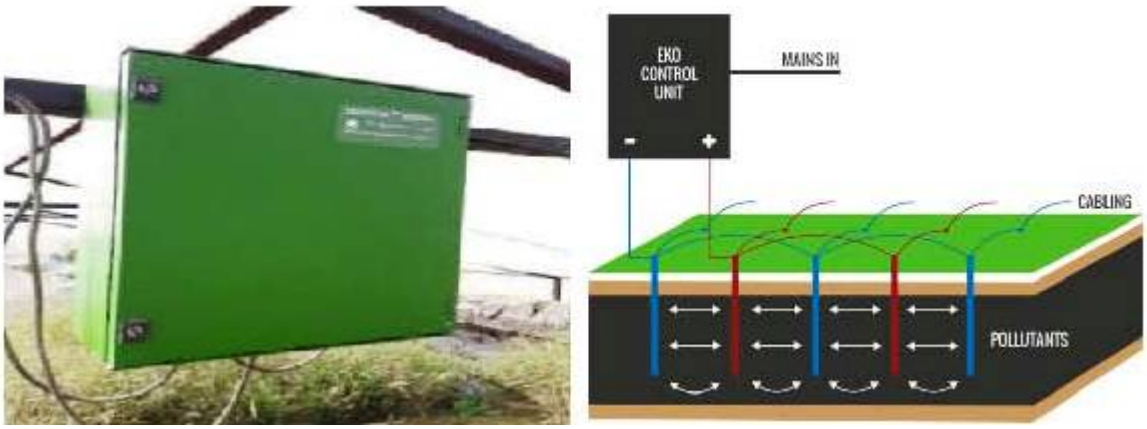


Fig. 4 EKOGRID™ Control unit on a site in Ecuador [5]

Technology Differentiation and Sustainability

Although the reactions described in the above section are typical for all treatment methods that are based on oxidizing and advanced oxidation processes, the results when utilizing EKOGRIDTM are achieved without the use of harmful chemicals. As the pollutants are remediated in-situ (not transported or relocated) and no chemicals are used in the process, there is also no secondary pollution as a result of utilizing the EKOGRID™ system.

Because of the extremely low operation voltage and very low current densities applied, EKOGRID™ causes no hazard or danger to humans, flora, or wildlife. In fact, after installation, normal daily activities can continue, allowing remediation to be carried out simultaneously with construction or daily operation activities on site. This low amount of energy consumption also allows the use of alternative energy sources, such as solar panels or wind turbines, to power the entire remediation process as long as a backup power source is available.

One single treatment is sufficient to obtain the decontamination of both groundwater and soil. Since this can take place in-situ, the expenses due to excavation, storage,

final processing or removal of polluted soil, or acquisition of clean replacements will be greatly reduced or become not necessary at all.

Nanotechnologies

Nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants which have limited remediation alternatives, avoiding degradation-related intermediates and increasing the speed at which degradation or stabilisation can take place. Between 2013-2017, the NanoRem[6] project carried out an intensive development and optimization program for different nanoparticles (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact.

Several media, as showed in Fig. 6 can be treated.

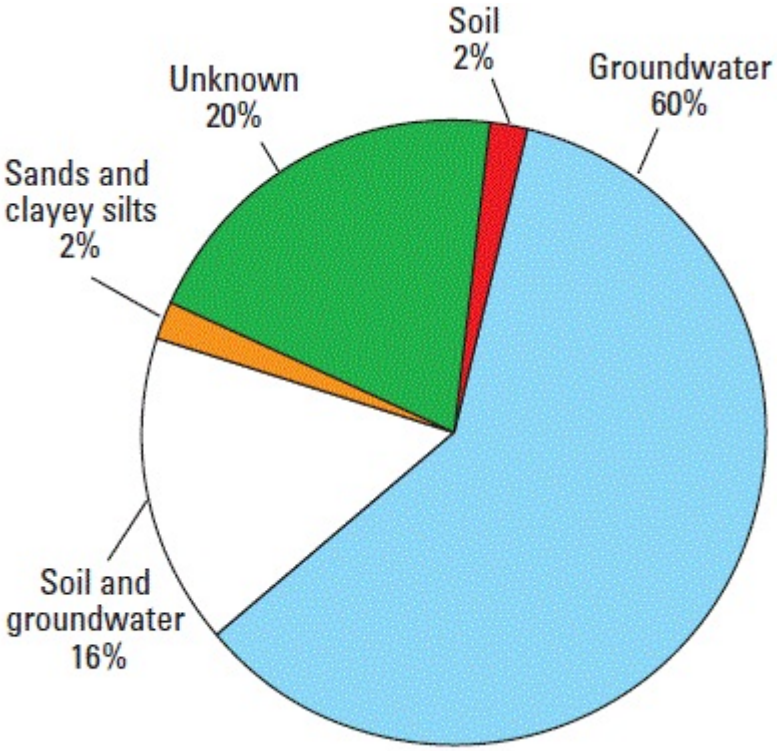


Fig. 5 Type of media treated with nanoparticles

Because many of the remediation projects using nanoparticles are just beginning or are ongoing, cost and performance data are limited. However, as the technology is applied at an increasing number of sites with varying geologies, more data will become available on performance, cost, and environmental aspects, thereby providing site managers and other stakeholders with additional information to determine whether the technology might be applicable to their specific sites.

Although the technology is likely a beneficial replacement of current practices for site remediation, potential risks are poorly understood. The factors and processes affecting ecotoxicity are complex, and knowledge of the potential impacts of manufactured nanoparticles in the environment on human health is still limited.

Nanomaterials have highly desired properties for in situ applications. Because of their minute size and innovative surface coatings, nanoparticles may be able to pervade very small spaces in the subsurface and remain suspended in groundwater, allowing the particles to travel farther than larger, macro-sized particles and achieve wider distribution. Many different nanoscale materials have been explored for remediation, such as nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals, titanium dioxide, zerovalentiron (nZVI)

Their active lifespan *in situ* is limited by a number of processes:

- ***Agglomeration*** – where nZVI particles are attracted to each other and aggregate into larger particles. In almost all cases this reduces their effective surface

area and their mobility in water.

- ***Passivation*** – where nanoparticle surfaces are chemically inactivated (although activity may remain within particles).
- **Immobilisation** in the aquifer solid matrix (e.g. through the processes of sorption).

These processes place limitations on treatment effectiveness by restricting the ability of nanoparticles to reach and treat contaminants *in situ*. To overcome these limitations, a number of modifications have been developed to improve the effectiveness of nZVI by reducing the scale of agglomeration and the immediacy of passivation. These include:

- Stabilisation – using a range of coatings, including biopolymers such as starch, chitosan, and carboxymethyl cellulose.
- Emulsification – where aqueous nZVI is surrounded by an oil-liquid.
- Anchoring nZVI onto carbon, cellulose acetate, polymeric resin or silica to prevent agglomeration and aid dispersion of the nZVI.

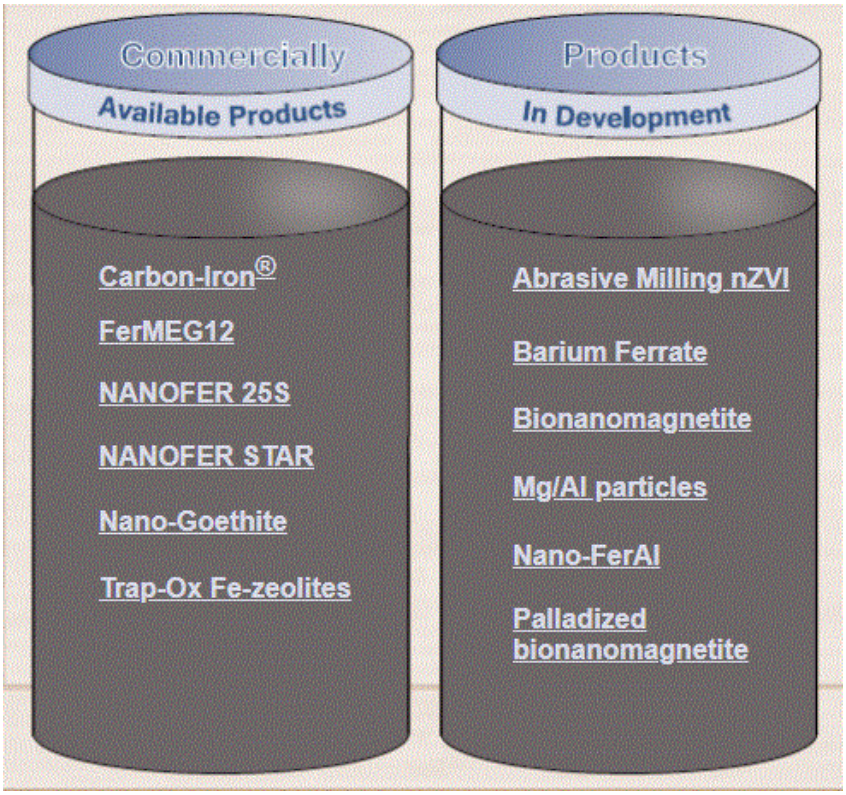


Fig. 6 Nanoparticles type

NanoRem has developed a range of nanoparticle types, some based on zerovalent iron and some not.

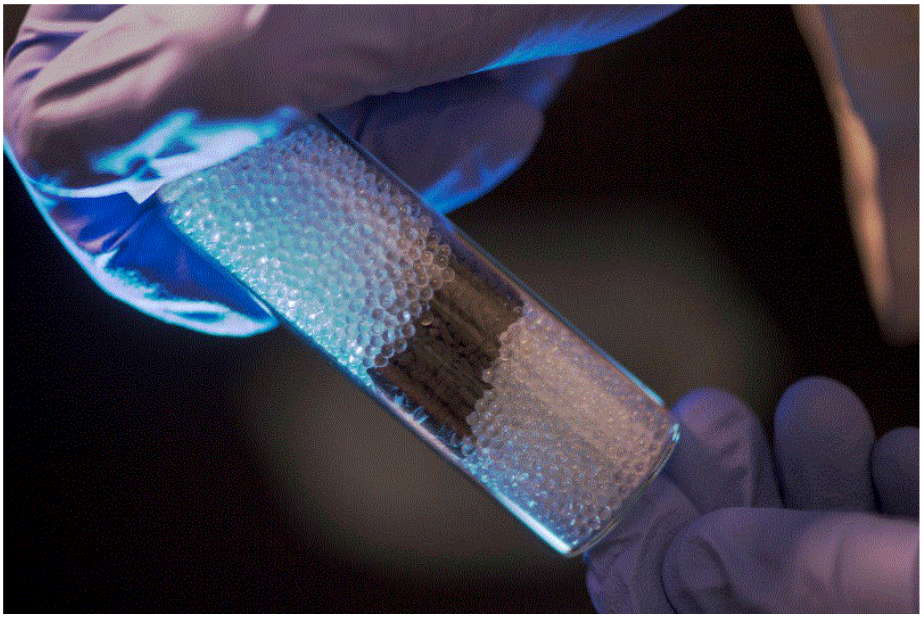


Fig. 7 Catalyst made with Nanoparticles

A catalyst made of nanoparticles of gold on aluminium atoms successfully treated chloroform-contaminated groundwater and is effective in treating other water contaminats such as nitrites and nitrophenol. [7]

Biosurfactants

Biosurfactants in the petroleum industry can be used in the cleanup of oils spills, the removal of oil residue from storage tanks, microbial-enhanced oil recovery, and the bioremediation of soil and water.

Biosurfactants are mainly produced by aerobic microorganisms in aqueous media with a carbon source feedstock, such as carbohydrates, hydrocarbons, fats, and oils.

These compounds have amphipathic molecules with hydrophobic

and hydrophilic portions that act between fluids of different polarities (oil/water and water/oil), allowing access to hydrophobic substrates and causing a reduction in surface tension, an increase in the area of contact of insoluble compounds (such as hydrocarbons) and the enhancement of the mobility, bioavailability, and biodegradation of such compounds.

Biosurfactants offer a number of advantages over chemical surfactants, such as biodegradability due to their simple chemical structure, environmental compatibility, low toxicity. Table 3 offers a list of biosurfactant applications in the oil industry.[8]

Step In Petroleum Production Chain	Applications
Extraction	• Reservoir wettability modification • Oil viscosity reduction • Drilling mud • Paraffin/asphalt deposition control • Enhanced oil displacement • Oil viscosity reduction
Transportation	• Oil viscosity reduction • Oil emulsion stabilization • Paraffin/asphalt deposition
Oil tank/container cleaning	• Oil viscosity reduction • Oil sludge emulsification • Hydrocarbon dispersion

Tab. 4 Common Application of biosurfactants in the petroleum industry

Since biosurfactants are not yet competitive with chemical

surfactants from the economic standpoint, a more thorough investigation of biosurfactant production from agro-industrial waste is needed to reduce the production cost and allow the large-scale production of these natural compounds. The versatility and efficiency demonstrated in the application of biosurfactants in the oil production chain and the removal of hydrophobic contaminants make these compounds promising biomolecules.

Phytoremediation

Phytoremediation is a set of processes that uses plants to remove, transfer, stabilize and destroy organic/inorganic contamination in ground water, surface water, and leachate. There are several ways plants can be used for the phytoremediation. These mechanisms include enhanced rhizosphere biodegradation, hydraulic control, phyto-degradation and phyto-volatilization.

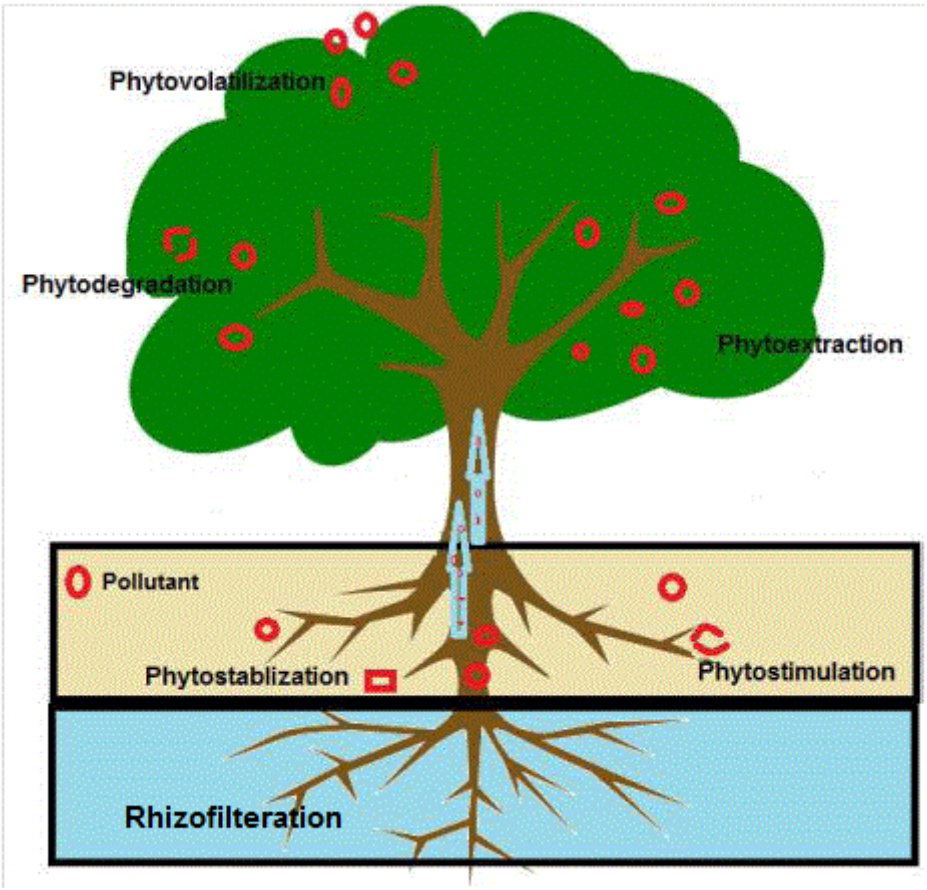


Fig. 8 Phyremediadion forms International [9]

This process can take several forms:

- Phytoextraction – uptake and concentration of substances from the environment into the plant biomass.
- Phytostabilization – reducing the mobility of substances in the environment, for example by limiting the leaching of substances from the soil.
- Phytotransformation – chemical modification of environmental substances as a direct result of plant metabolism, often resulting in their inactivation, degradation (phytodegradation) or immobilization (phytostabilization).
- Phytostimulation – enhancement of soil microbial activity for the degradation of contaminants, typically by organisms that associate with roots. This process is also known as rhizosphere degradation.
- Phytovolatilization – removal of substances from soil or water with release into the air, sometimes as a result of phytotransformation to more volatile and / or less polluting substances.
- Rhizofiltration – filtering water through a mass of roots to remove toxic substances or excess nutrients. The pollutants remain absorbed in or adsorbed to the roots.

There are a number of limitations to phytoremediation, such as:

- It is limited to shallow soils, streams, and ground water.
- High concentrations of hazardous materials can be toxic to plants.
- It involves the same mass transfer limitations as other

biotreatments.

- Climatic or seasonal conditions may interfere or inhibit plant growth, slow remediation efforts, or increase the length of the treatment period.
- It can transfer contamination across media, e.g., from soil to air.
- It is not effective for strongly sorbed (e.g., PCBs) and weakly sorbed contaminants.
- Phytoremediation will likely require a large surface area of land for remediation.
- The toxicity and bioavailability of biodegradation products is not always known. Products may be mobilized into ground water or bioaccumulated in animals.

More research is needed to determine the fate of various compounds in the plant metabolic cycle to ensure that plant droppings and products manufactured by plants do not contribute toxic or harmful chemicals into the food chain or increase risk exposure to the general public.

Radio-Frequency Heating

Radio-frequency heating (RFH) uses a high frequency alternating electric field for in situ heating of soils. The technique depends on the presence of dielectric materials with unevenly distributed electrical charges. The application of an electric field produces movement of the “polar” molecules, and this vibration creates mechanical heat. A spread of radio frequencies (e.g., 6.78 MHz, 13.56 MHz, 27.12 MHz, and 40.68 MHz along with seven higher frequencies) regulated and assigned by the Federal Communications Commission (FCC) can be used in industrial, scientific, or medical applications.

A radio-frequency heating system usually consists of [10]:

- A three-phase power supply.
- A radio-frequency source with an oscillator that generates a low-power current at the desired radio

frequency, several serial amplifiers that increase the strength of the oscillator current, and a final amplifier that delivers the current at the prescribed output level.

- An applicator system consisting of electrodes or antennae.
- A monitoring control system.
- A grounded metal shield over the treatment area.
- A vapor collection and treatment system

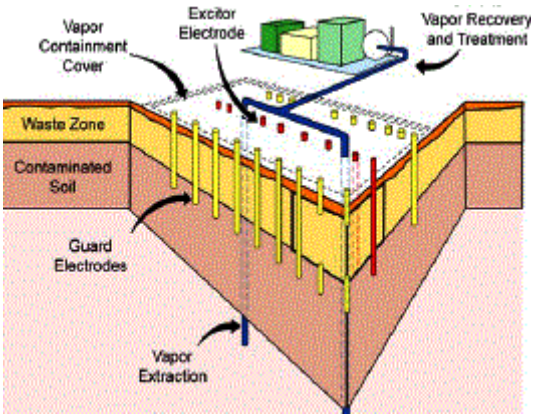


Fig. 9 Radio-Frequency Heating with Electrode

Early lab-scale experimentations demonstrated the possibility of heating up reservoir materials well above water boiling temperature by applying RF irradiation, and studied the effect on the temperature increase rate and on the oil recovery of factors such as temperature, pressure, connate water salinity, and solven injection. Lab-scale experimentations suffer from the impossibility to scale down geometrically the irradiation process, since electromagnetic irradiation at RF frequency is characterized by very long wavelengths, incompatible with small volume tests, while by changing the frequency, both reservoir permittivity and temperature profile change abruptly. Thus, field experiments are necessary for the experimental determination of the temperature profiles

arising from RF downhole irradiation, but really few data are available, due to the high costs associated.

With respect to other thermally enhanced remediation techniques such as steam injection, resistive heating or conductive heating, ISRFH has two main advantages:

- the heating rate is much higher and the temperature profiles more uniform, independently from soil geology;
- there is no fluid injected into the polluted soil, and thus the risk to enlarge the contamination to surrounding areas is minimized.[11]

---

[1] *http://www.responsiblebusiness.eu/display/rebwp8/Classification+of+remediation+methods*

[2] https://clu-in.org/download/toolkit/inchem.pdf

[3] *http://web.engr.oregonstate.edu/~hambydm/papers/remedrev.pdf*

[4] *http://web.engr.oregonstate.edu/~hambydm/papers/remedrev.pdf*

[5] *http://www.ekogrid.fi*

[6] http://www.nanorem.eu/

[7] *https://www.spe.org/en/jpt/jpt-article-detail/?art=2862*

[8] *Applications of Biosurfactants in the Petroleum Industry and the Remediation of Oil Spills, Int. J. Mol. Sci. 2014, 15, 12523-12542; doi:10.3390/ijms150712523*

[9] Journal of Environmental Bioremediation & Biodegradation. 2014, 2(4), 178-191 doi:10.12691/ijebb-2-4-5

[10] *https://nepis.epa.gov*

[11] Thermal Treatment of Hydrocarbon-Impacted Soils:A Review of Technology Innovation for Sustainable Remediation; Engineering 2 (2016) 426–437