

THE CHEMICAL TECHNOLOGIES OF SOIL'S DECONTAMINATION

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Abstract: The chemical soil degradation technologies are based on the pollutant conversion and immobilisation, or the mobilization, extraction and washing of pollutants. They use chemical agents that oxidize or reduce pollutants to less toxic or non-toxic forms and immobilize them in the underground environment in order to diminish their migration and the extent of pollution. Classification of chemical methods of depollution is based on the dominant reaction criterion: oxidation, reduction, neutralization, precipitation, chemical extraction, hydrolysis, dehalogenation, precipitation.

Keywords: technologies, chemical, soil, decontamination

1. INTRODUCTION

Chemical methods for soil degradation have purpose separating, destroying, immobilizing or transforming pollutants into less harmful forms by causing chemical reactions between pollutants and certain chemical reagents.

Classification of chemical methods of depollution is based on the dominant reaction criteria: oxidation, reduction, neutralization, precipitation, chemical extraction, hydrolysis, dehalogenation, precipitation.

Soil chemistry techniques act in two directions through different processes, but from the point of view of the installations and equipment used are similar.

2. CLASSIFICATION OF CHEMICAL DEPOLLUTION TECHNIQUES

2.1. Technics based on the transformation and immobilisation of pollutants

- the use of chemical agents that oxidize or reduce pollutants to less toxic or non-toxic forms and immobilises them in the underground environment in order to diminish their migration and the extent of pollution
- reduction agents are: sulfur dioxide, sulphites, metallic iron, zinc and ferrous sulphate
- techniques based on chemical oxidation destroy organic contaminants (pesticides) dissolved in the underground water, adsorbed or absorbed on the solid matrix of the aquifer or present in the free phase (gasoline)
- the oxidizing agents are: hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), ozone (O₃), persulfate (Na₂O₈S₂), perozone (ozone compound and hydrogen peroxide)

2.2. Technics based on mobilization and extraction (washing) of pollutants

- consist of feeding the polluted underground environment with chemical agents for the mobilization and dislocation of the pollutants by them, in the natural water stream or with an artificially amplified hydraulic gradient through suction activities - underground water injection
- groundwater pumped to the surface is treated ex-situ and reintroduced into the circuit

- chemical agents are introduced underground through injection wells, drains or infiltration basins (reduce pollutant interfacial stresses - a solid matrix of the underground environment, reduce surface tensions of pollutants, favoring the decrease of the volume of liquid pollutants immiscible with groundwater, increase the solubility of pollutants and diminishes their viscosity)
- transport of pollutants through the solid matrix pores, to suction or suction pumps
- chemical agents used for washing the solid matrix of the underground are:
 - detergents - the molecules facilitate the increase of the water solubility of the pollutants, dissolving them in the underground current
 - co-solvents - in contact with water, increase the solubility of some organic compounds

3. OXIDATION

In Situ Chemical Oxidation = the procedure in which a chemical oxidant is introduced into the site's subsurface with the purpose of transforming groundwater or soil pollutants into safer species. Through chemical oxidation, the oxidation state of a substance is decreased by accepting an electron to oxidize the target species. The target species is then put in a oxidized state which can eliminate the toxicity of the original contaminant (organic chemicals). To choose the oxidant, it is necessary site characterization, soil properties, hydrogeology, and geochemistry (fig. 1)

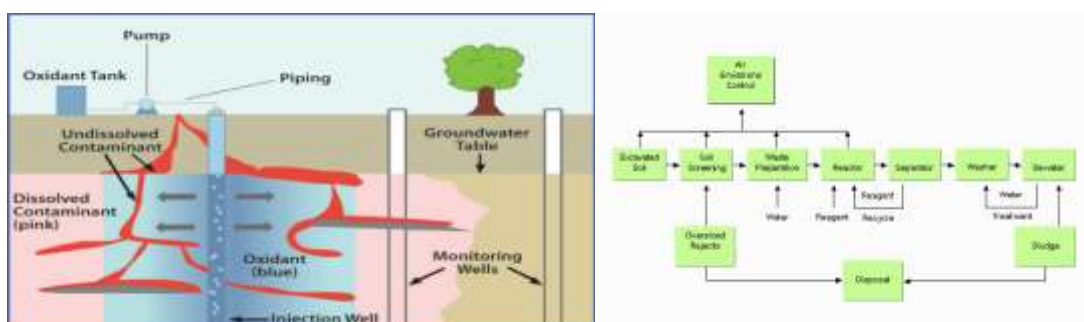
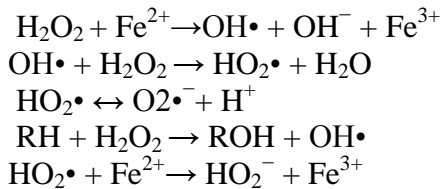


Fig. 1. The process of injecting an oxidant into a contaminated area

a. Hydrogen peroxide H₂O₂

- is a multi-action oxidant: it can degrade complex organic compounds, refractory to biodegradation (PCB, HAP); may alter the mobility of some metals; accelerates biodegradation of pollutants by increasing O₂ content
- the effect of hydrogen peroxide is catalysed by the action of ultraviolet rays
- in order for the hydrogen peroxide to be used as soil oxidizing agent, it must meet the following conditions: be well aerated, poor in organic matter, contain Fe⁺² ions in a reduced proportion (for oxidant to be consumed for conversion of Fe⁺² into Fe⁺³), does not contain the aldrin pesticide (which, by oxidation, turns into dieldrin, a degrading toxic product very slowly)
- the process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates or iron minerals, in order to produce strong oxidant hydroxyl radical (OH•) and other reactive oxygen species, through Fenton's initiation reaction



- the hydroxyl radical is one of the strongest oxidants found in nature, but it uses other species produced by subsequent chemical reactions of hydroxyl radical with hydrogen peroxide: superoxide anion ($\text{O}_2\cdot^-$), perhydroxyl radical ($\text{HO}_2\cdot$) and hydroperoxide anion (HO_2^-) (reactions producing these four species can degrade almost any organic contaminant)
- the nature of catalyst, pH and hydrogen peroxide concentration greatly impact the process
- soluble iron (at neutral pH), iron chelates and iron oxide minerals (at acid pH) as naturally present usually act as catalyst in reactions
- increase the hydrogen peroxide concentration, will lead to further propagation reactions, which will produce more reactive oxygen species and increase the treatment effectiveness

b. Permanganate MnO_4^-

- is a highly oxidized form of manganese, that serves as a selective chemical oxidant
 - is a powerful oxidizing agent that reacts quickly with pollutants and natural soil organic matter because 80% of the total amount of reacted potassium permanganate is consumed within one week
 - degrade the monounsaturated aliphatic halogenated organic compounds
 - potassium permanganate and sodium permanganate are the sources of the chemical used
 - the water solubility of permanganate depends on the medium temperature, size of crystal, extent of agitation and concentration
- $$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$$
- permanganate is highly reactive with alkanes and it is used to oxidize chlorinated ethenes, dichloroethylene isomers, vinyl chloride, phenols and polyaromatic hydrocarbons, but it is ineffective in oxidizing chloroalkanes, benzene and other aromatic compounds with low degrees of ring activation (fig. 2)
 - the cation associated with the permanganate (sodium or potassium) does not have a big influence on its oxidizing capability, but only the permanganate concentration

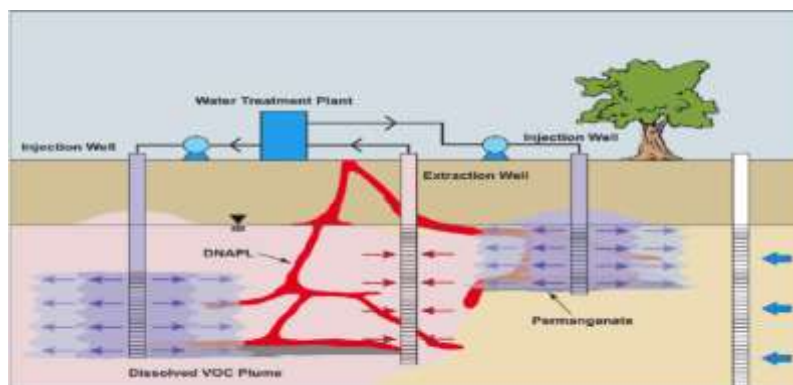
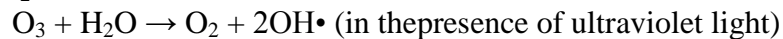
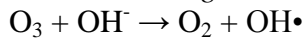


Fig. 2. Permanganate in situ oxidation application

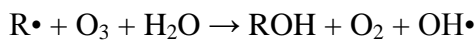
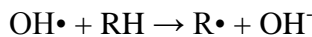
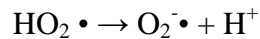
c. Ozone O₃

- is one of the strongest oxidants available for soil remediation (it is composed of dry air or O₂, which is inputted into an ozone generator and charged with a high voltage or UV irradiation, where O₂ molecules can be split and react quickly to form O₃; due to the instability of ozone, this must be generated on site)
- is used for the direct degradation of organic compounds
- ozone oxidation chemical reactions are:
 - ✓ direct oxidation (involves the oxidation of the targeted chemical by ozone in one reaction and it does not rely on the hydroxyl radical OH•)
 $O_3 + RC = CR \rightarrow RCOCR + O_2$ (*direct ozone reaction*)
 - ✓ indirect oxidation (includes chain-initiating reactions, chain-propagating reactions and chain-terminating reactions; is a faster reaction than direct oxidation due to the formation of the hydroxyl radical which rapidly attacks organic contaminants and breaks down their organic carbon-to-carbon bonds)

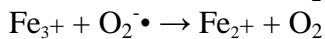
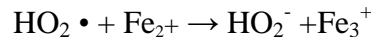
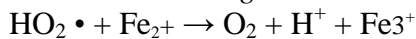
Chain-Initiating Reactions



Chain-Propagating Reactions



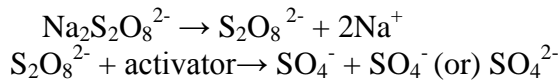
Chain-Terminating Reactions



- the ozone can be applied in situ in two forms: the injection of ozone gas and ozone sparging below the water table; are produced the injection of mixture of air and ozone gas directly into the unsaturated and saturated zones; depending on the reactivity and concentration of reactants, temperature and pH, contaminant oxidation will vary significantly
- the transport of ozone in unsaturated porous media is influenced by the water content, organic matter in the soil and metal oxides in the soil: the higher the water content, the quicker the transport; in increase in content of organics and metal oxides decrease the transport

d. Persulfate Na₂S₂O₈

- the three persulfate salts most commonly used are ammonium persulfate, sodium persulfate, and potassium persulfate; due to its solubility and content, sodium persulfate is the most widely used oxidant among them; oxidation can occur via electron transfer or free-radical pathways



- the solubility of persulfate, indicates that once injected, its transport mechanism will be dominated by density-driven and diffusive transport in low-permeability materials, it is more stable in the subsurface than other oxidants, with a half-life of 100 -500 days, it has the ability to be prominent in the system to further decontaminate an area for a longer duration
- unlike permanganate, it can oxidize benzene so it can be used in the remediation of fuel spills and benzene, toluene, ethylbenzene and xylene
- the need for sodium peroxide sulphate is 50% lower than the need for potassium permanganate
- pollutant removal rates vary depending on the initial dose of added oxidant
- the natural matrix of soil has a minimal influence on the oxidation reactions of the pollutants with sodium peroxide sulphate
- it is usually applied through direct injection or through horizontal or vertical recirculation wells

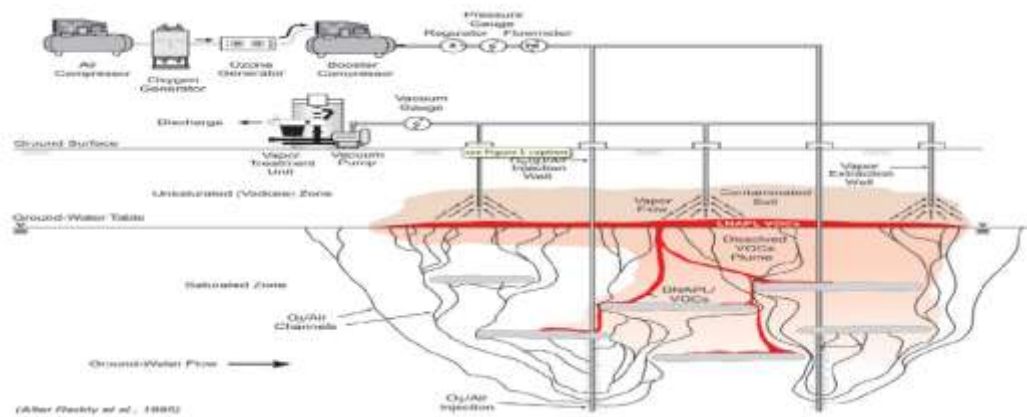


Fig. 3. In-situ ozonation in the saturated zone with soil vacuum extraction to capture volatile emissions

4. Reducing

For the decontamination of soils polluted with HCH by chemical reduction, iron is used, which has a double role:

- participate in degradation by degradation of hexachlorocyclohexane isomers
- creates anaerobic environmental conditions, optimal lindane biodegradation by sequestration of soil oxygen

5. Solvent extraction

The principle of the method - separation of pollutants from the contaminated environment by means of chemical reagents, appropriate to the type of pollution (solvents, acids, bases), followed by the recovery of reagents and the destruction of pollutants by other processes.

The pollutants that can be extracted by this method are: heavy hydrocarbons, tar, polycyclic aromatic hydrocarbons (HAP), polychlorinated biphenyls (PCBs), organic pesticides.

Solvent extraction is the most commonly used method and is carried in special reactors by using:

- standard solvent (alkane, alcohol, ketone) - the solvent is mixed with the excavated soil until a sludge is formed and float depollution
- liquid solvent - at the limit of saturated vapor pressure
- solvent whose solubility depends on the temperature - the pollutant concentrates obtained by these processes are destroyed, isolated or revaluated, using thermal methods, isolation in controlled deposits, electrolysis (fig. 4)

When the soil enters an extractor (a tank where the contaminated soil is mixed with the solvent), the soil is separated into three components or fractions:

- solvent with dissolved contaminants
- solids
- water

Different contaminants concentrate in different fractions: polychlorinated biphenyls (PCBs) concentrate in the contaminated solvent, metals in the solids and water.

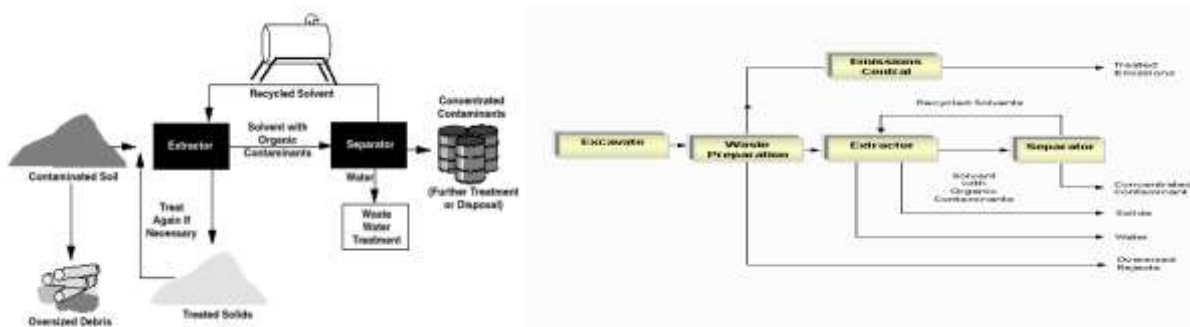


Fig. 4. The Solvent Extraction Process

CONCLUSION

- Classification of chemical methods of depollution is based on the dominant reaction criteria: oxidation, reduction, neutralization, precipitation, chemical extraction, hydrolysis, dehalogenation, precipitation.
- In situ chemical oxidation is the procedure in which a chemical oxidant is introduced into the site's subsurface with the purpose of transforming groundwater or soil pollutants into safer species.
- The oxidizing agents are: hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), ozone (O₃), persulfate (Na₂O₈S₂), peroxone (ozone compound and hydrogen peroxide).

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