C.3. Soil

Thermal Desorption Technology treatment of obsolete pesticides followed by integrated revitalisation

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Introduction

At former production sites, improper storage facilities and in their immediate surroundings, complex toxic compounds of obsolete pesticide contaminate soils. Also in pesticide contaminated diffuse soil the toxic substances have tendency for accumulation, without degradation, to reach low and medium concentration levels. These toxic substances penetrate the soil matrix with different flow rate, composition and concentration. They are either adsorbed on the outer surface of the soil particles or sorbed into the internal structure of the soil. Pesticide contamination in soil prevents proper utilisation of valuable land, decreases agricultural production, polluting groundwater and exerts direct impact on the humans and animals.

Pesticides and other organic micropollutants can be found as cations, anions, polar or apolar molecules in the soil matrix. The cationic pesticides are good water-soluble and strongly bound to the soil colloids. In acidic soils, the ion exchange capacity decreases; therefore the adsorption capacity is also decreasing, while in the neutral and alkaline soils the adsorption increases. The weak bases in acidic environment have cationic forms, while the weak acids in alkaline soils have anionic forms. The soil colloids have negative charge and repel anionic molecules. The apolaric pesticide molecules have low solubility in water and primarily well bound into the soil humus fraction.

The transformation of pesticides molecules is a complex, chemical physical and biological, process. The rate of pesticides transformation is highly dependent on the soil characteristics. In acidic soil, the degradation is decreased or prevented. Some fungi, such as *Fusarium, Aspergillus, Penicillium, Alternaria, Trichoderma, Gliocladium, Candida*, and bacteria such as *Methanobacterium, Clostridium, Enterobacter, Pseudomonas, Bacillus, and Aerobacter*, have active transforming mechanisms. The micro-organisms may use the pesticides as substrate with the subsequentvariable degradation degrees. However, in most cases, high concentrations of the pesticides are bioaccumulated in the microorganisms reaching in some cases several hundred times versus the environmental levels. Therefore, the removing process of the pesticide is only temporary and a potential toxic effect is still remaining.

Often biological soil degradation or decontamination methods are not viable because of the complex chemical structure of the pesticides at production sites and storage facilities, whereas different types of pesticides are present in the contamination matrix. Therefore, by means of the sole application of biological degradation methods, the results are difficult to predict and control, followed by high cost. The pollutant must be in a chemical state conductive to microbial utilisation and in an aqueous phase to enter a microbial cell and be biologically available for degradation. Many pesticides (e.g. chlorinated hydrocarbons - DDT, gamma HCH, hexachlorobenzene) are only slightly soluble in water. These hydrophobic pesticides tend to persist in nature, highly adsorbed to organic solid particles resulting in accumulation in soil. The major problem of biological transformation of pesticides is not only the very slow degradation, but also the produced degradation xenophobic toxic and non-biodegradable metabolites (e.g. carcinogenic metabolites from aldrin and heptachlor biodegradation), which are more toxic than the parent compound.

In many cases incineration is used for soil decontamination. However, application of the directly heated thermal treatment systems, such as incineration or gasification in partial oxidative environment, results in oxidation of the inorganic parts of the complex soil substance as well. In these cases the organic contamination and substances with volatile parts will be burned out. However, the natural inorganic soil substance, which is the main fraction, will be oxidised as well generating more and different types of toxic components than the original contamination itself, e.g. the result is dead soil.

Owners of contaminated land are deeply concerned about

- the exact predictable time frame of the decontamination procedure (desirable 1-2 years),
- financial, business, legal and technical risks taken,
- the guaranteed end result of the decontamination procedure with total solution,
- the fixed cost frame and total cost efficiency,
- the legal responsibility and legal acceptance.

In many cases biological degradation methods are not viable or only partially efficient, especially in situations when

- the contamination is of heavy oil character,

- the contamination containing persistent and halogenated compounds,
- the contamination is concentrated, and
- there are concerns about the toxic residual substances after biological remediation.

By the directly heated thermal treatment of the soil, such as incineration or gasification in partial oxidative environment, the complex substance is partially oxidised, whereas

- the organic contamination and substances will be burned out, however
- the natural inorganic soil substance will be partially oxidised as well, whereas
- the oxidation process is generating other unwanted toxic components than the parent contaminant resulting in dead soil with low opportunity of recultivation.

The solution

General

Final elimination of pesticide contaminated substances with variable toxic composition, concentration and flow at former production sites, improper storage facilities and in their immediate surroundings takes place using indirect low temperature thermal decomposition. Complete reductive environment and vacuum are achieved with gentle removal of volatile contaminants. The treated substance is not oxidised, whereas inorganic components are not changed. Gas vapours are burned out in high temperature with a minimum of 2 seconds residence time, the off-gas is cleansed, while the solid phase is renaturalised by TDT-3R™ integrated biological revitalisation by determined microbiological species for comprehensive post processing. A mobile unit is designed and prepared for field and full scale demonstration with continuous throughput capacity of approximately 1 m^3/h and 2,5 m^3/h. Applied patent: US 5,707,592, Jan. 13, 1998.

TDT - 3R™ main process

The main component of the Thermal Desorption Technology Recycle-Reduce-Reuse Terra Humana "TDT - 3R™" is a specially designed, indirectly fired, horizontally arranged rotary kiln reactor. In the reactor, the contaminated soil in a reductive environment is gased-out under low vacuum (0-50 Pascal) and a material core temperature range of approximately 300ºC - 350ºC.

Gas vapour from the thermal desorption process is directly combusted at a minimum temperature of 850 ºC (for organic contamination) or 1,250 ºC (for halogenated contamination) with a minimum of 2 seconds residence time, fast cooled and heat from its flue gas is recovered. In the case of halogenated contamination, it is generally experienced that dioxin and furan gases are not created/recreated in a reductive environment and the pyrolysis gas-vapour phase does not contain dioxin-furan gases. The remaining gas is cleansed in an efficient high capture wet gas multi venturi scrubber prior to discharge. Scrubber process water is cleansed prior to discharge and the neutralised precipitate with the water from treatment are disposed off site on a permitted landfill.

The cleansed soil is indirectly cooled and discharged containing outgased porous carbon char, which during the recultivation phase will keep the moisture content and provide protected sites for implanted micro-organisms.

Process technical aspects

- High efficient heat transfer to the basic material, such as the horizontally arranged kiln,
- Revolutionary technical solution for the rotary kiln sealings between the moving and stationary parts,
- Advanced technical solution for the continuous throughput of the feed stock,
- Advantageous and safe application for high concentrated (>10,000 mg/kg) contaminated soil treatment
- Flexible operations: operates in a range of 25 % to 125 % of nominal capacity,
- Closed continuous input - output system,
- Simple - safe vacuum system, easy start up - shut down,
- Total heat recovery,
- The TDT - 3R™ rotary reactor system is of a simple technical - mechanical construction, containing no exotic technical construction and exotic materials,
- Mobile version is available,
- Throughput capacities of: 2 t/h, (15k-tpa) or 5 t/h, (36k-tpa), larger capacities are also available.

The TDT-3R™ is the advanced answer for these environmental challenges beyond year 2000. It meets the U.S. RCRA Miscellaneous Units 40 CFR 264 Subpart X for Thermal Desorbers and compatible E.U. Norms for Thermolysis. It has the following main characteristics:

- Thermal Desorption Chamber: indirect-fired heat source used for primary desorption chamber with relatively low operating temperature,
- Air Pollution Control Devices "APCD": non-destructive APCD is used,
- Waste Residual Management: treatment of residuals is separated from the thermal desorber.

Pilot tests have been executed during 1993/1995 with a feed capacity of approx. 150 kg/h and soil moisture content averaged 26 %.

Table 1. Results of pilot test during 1993/1995

Contaminant	Feed soil concentration mg/kg	Treated soil concentration µg/kg	Removal Efficiency %
Benzene	51	50,55	99,12
Toluene	47	46,5	98,95
Ethylbenzene	185	184,6	99,81
Xylenes	556	555,1	99,85
Naphthalene	1354	1353,4	99,96
2-Metylnaphtalene	3458	3457,6	99,99
Phenanthrene	541	540,3	99,88
Anthracene	344	343,6	99,91
Pyrene	58	57,5	99,29
Benzo(a)Anthracene	76	75,4	99,32
Chrysene	49	48,6	99,34
Styrene	15	14,9	99,43

The characteristics of the TDT-3R™ treatment process allow heavy metals and volatile compounds to be separated into two separated flows under the complete reductive thermal decomposition process with vacuum and less than 500 ºC treatment temperature.

The main thermal desorption - thermolysis process avoids creation of dioxin D and furan F gases by its nature. Furthermore, the re-creation of D/F is avoided by the construction design, flux of soot and particles into the gas-vapour phase, imperfect burn out of organic components in the post combustion phase, flux of heavy metals into gas-vapour phase, oxidation of heavy metals in the solid phase, and creation of NO_x, SO_x, CO and CO_2.

The status of the TDT-3R™ technology

The TDT-3R technology has successfully passed the scientifically research and pilot scale tests, whereas concept, method and apparatus have been worked out. Field demonstration plant with 1 m^3/h continuous throughput capacity and full scale plant with 2,5 m^3/h throughput capacity engineering design has been executed in detail with alternative industrial applications. The status of the TDT-3R technology is a post innovative phase and a prior field scale demonstration phase.

Controlled revitalisation of TDT-3R™ treated clean soil for the use as top soil (< 1 m)

Soil is a highly complex system characterised by a variety of biological, chemical and physical processes, which are highly influenced by the environmental factors. Micro-organisms inhabit soil and, together with exocellular enzymes and the soil mesofauna and macrofauna conduct all the known metabolic reactions. Micro-organisms play a key role in the decomposition of soil organic matter and nutrient cycling, and therefore microbial activity is most important for the maintenance of soil fertility. The integrity of the metabolic capacity of the soil microflora is a fundamental requirement for any concept of soil recultivation.

Figure 1. TDT-3R™ pilot plant

The TDT-3R technology removes organic and volatile pollutants from the contaminated soil at low temperatures and a reductive environment unlike the conventional burning processes where the environment is oxidative. Because of the reductive environment, the primary composition of the inorganic compounds of soil is unchanged but the biological system and the organic structure of the soil is changed. The treated soil is not a "dead soil", but suitable for revitalisation of the inorganic soil matrix under controlled and predicted conditions:

- after the TDT-3R™ treatment the soil lost the original organic compounds and the soil original structure has been changed,
- the composition of non volatile and the decay of inorganic compounds remained unchanged, but are not biologically available for the plants,
- the soil has a biologically inactivated carbon structure,
- the soil lost volatile compounds,
- the treated soil is dry since it lost the water contents,
- the soil lost most of the available nitrogen (organic nitrogen contents),
- the soil is biologically inactivated (sterile).

This treated soil has not got any biological activity and therefore this soil will not provide organic and inorganic nutrients for plants and soil organisms. Subsequently it opens a new opportunity for controlled recolonisation of the soil according to the needs. The following procedures will be considered for controlled soil revitalisation:

- Increasing the water contents of the treated soil

The treated soil is dried. The soil moisture is an important factor for the soil life since organic and inorganic nutrients are only available for micro-organisms and plants if they are dissolved in aquatic phase. We have to cool the hot treated soil with water. If the treated soil has small aquifer capacity, we have to mix it with an argillaceous mineral before adding water. Bentonite has a high adsorption capacity.

- Rebuilding the soil natural organic structure by providing organic and inorganic nutrients for soil micro-organisms.

The first and elementary step of the revitalisation is rebuilding the soil natural organic structure, by providing nutrients for soil micro-organisms and plants. Organic carbon, nitrogen, phosphorous, sulphur, potassium, calcium, magnesium and some micro-nutrients (ferry, manganese, copper, sodium, chlorine, boron, selenium) are the most important abiotic soil compounds which are essential for the soil life.

Organic carbon: organic carbon is essential for micro-organisms not only as a nutrient, but also as a physical soil conditioner that influences soil aggregation and water characteristics. Soil micro-organisms, together with the soil enzymes, hold a key position in the processes of humification and mineralisation of organic substrates, which lead to the production of persistent humus, degradable organic compounds and carbon dioxide.

Soil nitrogen: all the higher plants and micro-organisms depend on combined nitrogen for their nutrition. Combined nitrogen in the form of ammonia, nitrate and organic compounds, often becomes the limiting factor. The cyclic transformation of nitrogenous compounds, including the mineralisation of nitrogenous organic matter, is of great importance in the total turnover of this element in soil. Nitrogen mineralisation consists of two different processes: the ammonification of organic compounds by a large number of heterotrophic micro-organisms, and the oxidation of the released ammonia to nitrite and nitrate mainly by autotrophic bacteria. The mineralisation of organic nitrogen depends mainly on temperature, moisture, aeration, type of organic N and pH. The inorganic N produced by mineralisation is subject to N immobilisation and fixation by clays.

Micro-organisms are highly involved in the cycling of nitrogen in soil, because they carry out nitrogen fixation, nitrification, gentrification, and nitrogen mineralisation - immobilisation turnover. Total nitrogen analysis, the C:N ratio and the mineral N fractions (mainly ammonium and nitrate) provide insight into the N supply to microflora and plants, and thus reflect an aspect of the microbiological status of a soil. Ammonium and nitrate in the soil solution are the nitrogen sources of plants. Inorganic N is liberated by mineralisation of organic compounds or added to soil as fertilisers.

Soil phosphorus: Soil phosphorus is made up of an inorganic (bound or dissolved) and an organic fraction with varying percentages ranged between 5% and 95% of the total for each. Only a small fraction appears in the soil solution. Soil microbes are involved in the mineralisation of P from organic debris. Extracellular phosphates are produced by micro-organisms and plant roots and contribute to the mineralisation of organic P.

Soil sulphur: Sulphur exists in soil in solid or dissolved inorganic forms as sulphides or sulphate, in soil organic matter, especially in proteins, or in minor trace gases.

Supply of organic and inorganic components

- ***Mixing the treated soil with high humus containing natural soil***

  The soil humus fraction develops the soil natural structure, provides nutrients for micro-organisms and controls the soil water circulation. The natural humus soil contains the natural soil organisms - bacteria, algae, fungi, micro and macro animals - that are very important in the treated soil recolonisation. If we provide the organic and inorganic nutrients, the natural organisms will help to recolonise the treated soil.

- ***Mixing the treated soil with a biocompost***

  We can compost agricultural by-products. The criterion of the by-products selection is the organic content (min. 30%) and the C/N ratio (has to be 25-30:1). We inoculated the basic material with selected micro-organisms. The compost provides organic and inorganic nutrients for micro-organisms. The compost inorganic content depends on the basic material composition, but we can mix the basic material with a high inorganic contents stone (basalt, bentonite).

- ***Mixing the treated soil with alginate***

  Alginate has a high adsorption capacity (1 kg alginate can adsorb 1.0-1.3 l water), and contains 64 different micro and macro- nutrients. Alginate also has a high organic content 140-150 kg/ tonne). This material is excellent for soil micro-organisms and plants. Alginate is impregnated with selected and fermented liquid, containing controlled species.

Economic analysis

The economic analysis of the TDT-3R™ technology revealed that operating costs are mostly affected by the feed rate and residence time. Soil moisture content, soil treatment temperature (which is determined by contaminant type and concentration) and the cost of fuel are site-specific factors that effect costs. The soil moisture content determines the feed rate and residence time needed to proper treatment of the soil.

Contaminant related specific factors affecting costs:

- the volume of the contaminated soil
- the type and characteristics of the contaminated soil
- the type and characteristics of the contaminants ion
- the input toxic concentration of the contaminated soil

- soil moisture content (> 20 % to < 50 %), for sludge type < 75 %,
- treatment goals
- residual volume (depending on the pollution concentration and type, sludge from off-gas treatment is produced and removed to off-site disposal)
- regulatory permit requirements

Site related specific factors affecting costs:

- site area accessibility
- availability of utilities
- cost of natural gas or oil
- geographic location

For the treatment of 5,000 tonnes of hydrocarbon contaminated soil with an expected execution time of 6-8 months, a moisture content of approx. <25 %, with an average toxic concentration of approx. 15,000 mg/kg, the following cost factors (year 2000 basis) are considered and estimated:

- Site preparation and fencing costs
- Permitting and regulatory costs
- Equipment lease costs
- Start-up costs
- Labour costs
- Supply and consumable costs
- Utility costs
- Natural gas or oil fuel costs
- Residual management cost
- Equipment transportation costs
- Analytical costs
- Equipment maintenance and spare part costs
- Insurance costs
- Site demobilisation costs
- Financial reserves

Estimated thermal desorption treatment cost for 5,000 tonnes:

On this calculation basis, the estimated TDT-3R™ thermal desorption average treatment costs are: US$ 115-175 / tonne.

Estimated soil revitalisation post treatment add-on cost for 750 tonnes of topsoil cover: complex mixing the treated soil with high humus containing natural soil and/or biocompost and/or alginate is estimated to be: US$ 30-50 / tonne.

The results

- ***Short decontamination time***: Providing exact predictable and very short time frame of the decontamination procedure, which makes fast capitalisation of the remediated land and fast ending of owners' legal responsibility for pollution. The fast action also promptly stops further contamination to groundwater,
- ***Comprehensive solution***: Providing guaranteed end result of the decontamination procedure with complete solution,
- ***Advantageous and safe treatment of any concentration levels for complex soil pollutions***: advantageous and safe treatment of any concentration levels, but especially cost efficiently from the medium (3,000 - 15,000 mg/kg) and high concentrated (from 15,000 mg/kg) soil contamination, with complex chemical, biological and hydrocarbon pollutions,
- ***Topsoil revitalisation***: The total volume of contaminated soil is cleansed and the revitalised soil can be used as top-soil (< 1 m) under recultivation phase,
- ***Cost efficient with fix cost***: Providing fixed cost frame and total cost efficiency,
- ***Legal acceptance***: Providing full legal acceptance of the site decontamination procedure.