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Application of thermal desorption as treatment method for soil contaminated with hazardous chemicals

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Abstract. Soil is constantly evolving under the influence of both environmental factors and human activities. Because of strong industrialization in the past, Romania is among those European countries that have large areas contaminated by industrial waste, containing hazardous chemicals. The paper is an overview of thermal desorption methods used for the treatment of soils contaminated with hazardous chemicals such as mercury or DDT and will emphasize the optimal conditions for conducting thermal desorption.

Key words: thermal desorption, remediation, pollution sites.

Introduction. Thermal heating is a remediation process in which heat and vacuum are applied simultaneously to polluted soils. Thermal desorption is used in different ways, namely in situ or ex situ by thermal blankets placed on the surface of the soil, or by electrically heated vertical thermal bars that can reach temperatures of 800 – 900^{0}C. (Stegemeier & Vinegar 2001).

Persistent organic pollutants (POPs) are derived from a variety of activities (agricultural and industrial), are toxic chemical compounds that resist to biodegradation in biological environment and these compounds can be transmitted into the atmosphere or water on large distances.

The thermal treatment processes of soils contaminated with hazardous chemicals have been studied at a laboratory scale by Gasmer Shell Road and General Electric Corporate, research and development centers in Schenectady New York.

Both research used in situ thermal desorption with thermal blankets (quilts) and were proved to be very effective for the removal from soil of hydrocarbon, policlorbifenils, pesticides and chlorinated solvents. The treatment requires two to ten days depending on the pollutant’s depth in soil and on the soil moisture (Stegemeier & Vinegar 2001).

Thermal wells are installed in the ground, at 5-7 m distance. The depth of pollutants extraction can reach up to 30 m, being very effective in soils that are below different buildings.

At Missouri Electric Works, on the Superfund site, thermal wells were located which were heated with equipments at the temperature of 550^{0}C and maintained for 250 hours. The distance between heat pipes that have been placed in the soil was determined as 1.5 m.

The temperature increase determines the volatilization of volatile and semi-volatile organic compounds that are further absorbed by a vacuum pump. The cost of such a process is in the range of 50 $ to 250 $ per ton of soil (Stegemeier & Vinegar 2001).

In Romania there is a historical pollution in the area of the former chemical plant in Turda due to uncontrolled disposal of HCH and DDT wastes. Here there were identified six HCH landfill covering an area of over 7 ha which accumulate a quantity of about 15,000 tonnes of waste (Proorocu et al 2009).

Material and Method. Temperature levels needed for the desorption processes depend on the average molecular weight of the products to desorb (Fig. 1).

Polluted soil heating allows volatile compounds to escape through a process of thermal desorption of pollutants. In fact, the vapor pressure of pollutant adsorbed fractions increase when substrate temperature increases. This entails the migration of pollutants into the gas phase, desorbed vapors being extracted continuously.

Thermal desorption is generally performed in reducing atmosphere (oxygen below 2%), desorbed vapors being continuously extracted, thus moving desorption equilibrium in a favorable manner. Depending on the existing oxygen content in the desorption unit, partial oxidation processes of fuel vapor can occur. Also, depending on the temperature used, the internal pyrolysis processes can be observed.

Desorption vapors are generally directed to a downstream treatment device in which pollutants are being recovered (by condensation, adsorption on activated carbon) or destroyed (postcombustion). Gases are further filtered and treated (by dry or wet means) before being discharged into the atmosphere (Micle & Neag 2009).

In the case of soil contaminated with VOCs, thermal desorption is adequate if the soil has a moisture content of 10-15%, since water vapor can entail some of these compounds. After the performed analysis the optimal temperature for treatment of soils contaminated with pesticides, dioxins and PCBs by thermal desorption, was established to be in the range 450^{0}C – 500^{0}C (Prasek et al 2007).

Thus, thermal desorption processes currently allow obtaining remediation yields above 95%, depending on the applied temperatures and times. Optimum operational parameters of the process should take into account the kinetic limitations of the desorption process, depending on the couple substrate/pollutant and limitations of mass and heat transfer, depending on the substrate (particle size, humidity) and modes of heat transfer of the desorption unit. Particularly, the presence of a high initial humidity of the soil reduces the overall efficiency of desorption at the same period of treatment.. Therefore de-polluted soils are air or water cooled or in a cooling unit and rehumidified to avoid dust emissions (Micle & Neag 2009).

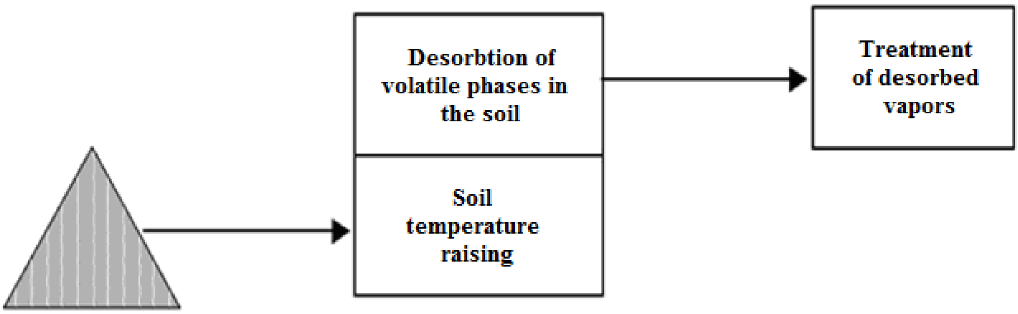

Figure 1. The principle scheme of polluted soil treatment by thermal desorption (Micle & Neag 2009)

Also, this method is effective for non-polar halogenated aromatic compounds (chlorobenzene, dichlorobenzene), phenols, nitrate compounds and PAHs (anthracene, biphenyl, chrysene, naphthalene, pyrene). On the contrary, levels of applied temperature may be insufficient for vaporization of cyclic aliphatic halogenated compounds (ethers, esters), certain halogenated compounds (PCBs, dioxins and furans).

Modes of heat and material transfer that are in place depend on the type of the desorption unit. Heat transfer mechanisms are shown schematically in Figure 2.

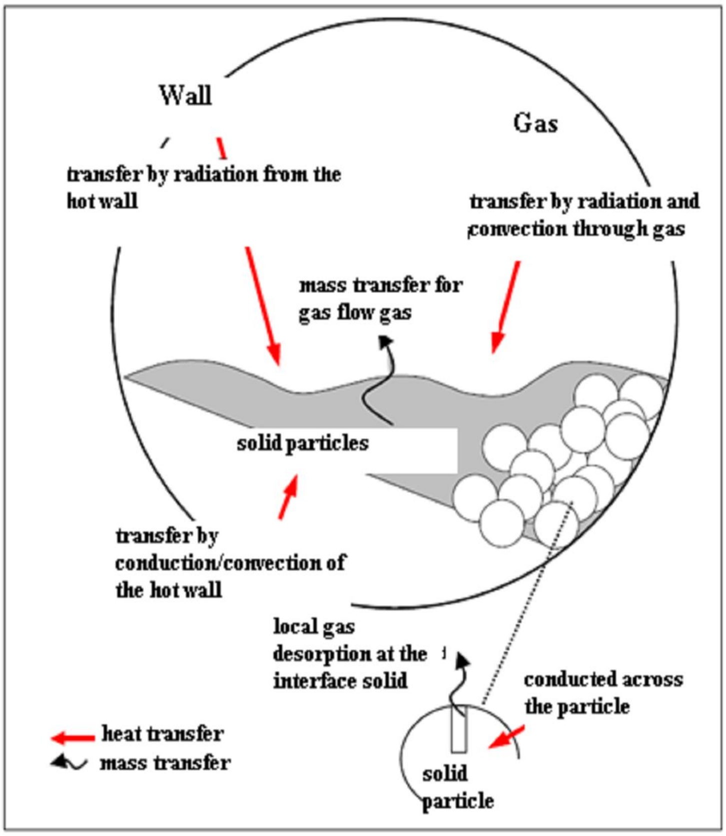

Figure 2. Transfer phenomena during desorption.

Decontamination of polluted soil is made by extracting volatile compounds from polluted soil by heating it in a stationary instalation, at a temperature that doesn't exceed 650^{0}C. Increasing the temperature creates an increase in vapor pressure and the pollutant, in solid or liquid phase adsorbed on the soil matrix passes into the gaseous phase (steam) (Micle & Neag 2009).

Before placing the soil inside the thermal desorption plant, it undergoes pre-processing operations such as crushing, grading and drying.

Desorption effectiveness depends on the temperature and the time the contaminated soil is kept inside the heating furnace. Operational parameters depend on the matrix torque soil/pollutant, mass and heat transfer limits, these depending on soil properties (particle size, moisture) and on heat transfer mode in the desorption unit.

Temperatures required for the desorption process depend on the average molecular weight of products subjected to desorption. There are two types of processes depending on the temperature level:

- *low temperature processes* (250 ÷ 450 ^{0}C) used for most volatile pollutants, whose advantage is to be less "aggressive" for soils;
- *average temperature processes* (450 ÷ 650 ^{0}C) used for heavier compounds; at this temperature along desorption the partial pyrolytic destruction of pollutants in soil components take place.

Ex situ thermal desorption. Desorption processes differ depending also on the mode of heat transfer:

- thermal desorption by direct heating;
- thermal desorption by indirect heating (Micle & Neag 2009).

The main advantage of ex situ treatments is that they generally require shorter periods of time, and there is greater certainty about the uniformity of treatment. However, ex situ processes require excavation of soil, which increases costs for desorption and equipment (Fig. 3). If soil moisture is higher, the costs increase due to additional heating (http://newlebanon.biz/Pages/C/C_06a3r.html). 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 (Pavel & Gavrilescu 2008).

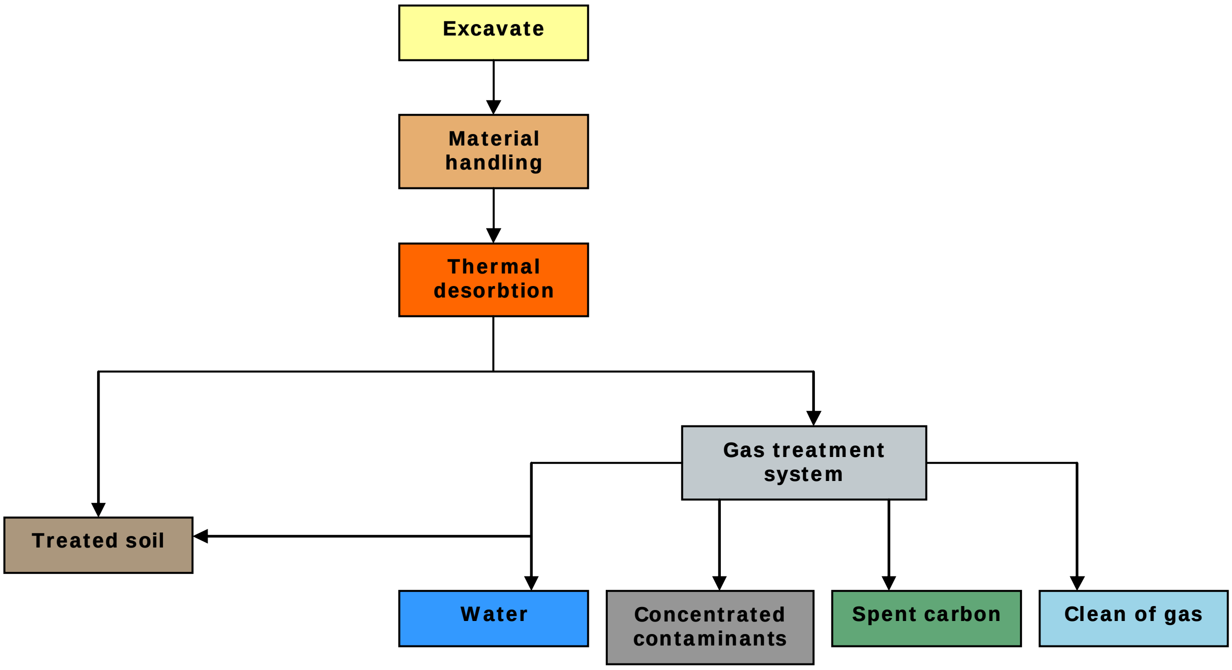

Figure 3. Schematic diagram of the ex situ thermal desorption (Pavel & Gavrilescu 2008)

Thermal desorption process by direct heating. Thermal desorption process with direct heating (Fig. 4) consists in the introduction of caloric energy through direct contact (convection and radiation) in the treated soil (matrix and pollutant). Heat is obtained using a burner (propane or natural gas) placed in the desorption chamber.

Gaseous pollutants are directed along with hot combustion gases to an additional gas treatment unit.

This type of process, with a large treatment capacity and relatively simple treatment in terms of design, is suitable for treating soils with moderate calorific power and soil humidity of 25% or less. Major drawback of this technique is the large volume of gas treated per unit solid mass (Micle & Neag 2009).

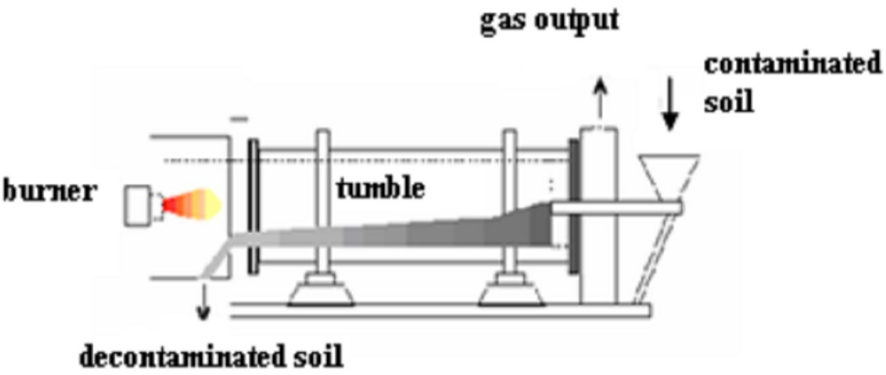

Figure 4. Scheme of desorption unit with direct heating (Micle & Neag 2009).

Thermal desorption process with indirect heating. Thermal desorption process with indirect heating consist in the introduction of caloric energy by conduction and passing it through another wall (double hot jacketed, electrical resistance) and by radiation from the hot wall (Fig. 5). Gaseous pollutants are directed to a desorbed gas treatment unit. This process has the following advantages:

- allows soil treatment regardless of calorific content;
- allows soil treatment even for soils with a high humidity;
- minimum quantities of treated gas result (fuel gas being unmixed with desorbed steam).

Biggest drawback of this technique is the limited treatment capacity.

The gases leaving the desorption unit are treated before discharge into the atmosphere by postcombustion, dusting and washing. After soil treatment by thermal desorption, decontaminated soil is cooled by air or water and rehumidified to avoid dust emissions.

Efficiency of pollutants extraction from the soil by thermal desorption is lower comparing to the efficiency of remediation by incineration.

Compared to incineration, thermal desorption requires lower costs and soil humic materials are not destroyed by burning (Micle & Neag 2009).

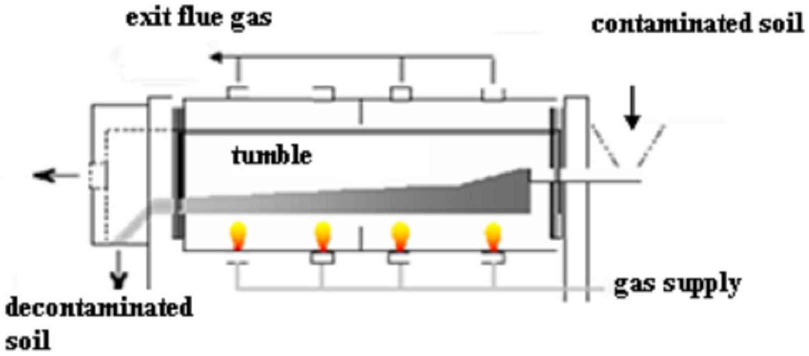

Figure 5. Scheme of desorption unit with indirect heating (Micle & Neag 2009).

Process effectiveness was demonstrated in the case of soils contaminated with volatile heavy metals such as mercury, and in the case of soils polluted with:

- halogenated on dehalogenated volatile or semi-volatile compounds (aliphatic: petrol, diesel);
- aromatic hydrocarbons: benzene, toluene, xylene, ethylbenzene, dichlorobenzene;
- phenols;
- nitrate compounds;
- PAH;
- PCB;
- pesticides;
- organic cyanides (Micle 2009).

Advantages:

- the main advantage of ex situ treatment is that it generally requires shorter periods of time;
- uniformity of the treatment;
- continuous soil mixing and stirring;
- the method can treat soils at different depths thanks to the excavation process.

Disadvantages:

- higher costs due to excavation;
- high risk due to transport of the contaminated soil to the thermal desorption unit.

In situ thermal desorption. It's a developing technology that allows treatment of soil and sediments by heating them by means of thermal blankets placed on shallow contaminated areas (<0.61 m) or through heated tubes for deeper contamination (Fig. 6).

The heat conduction process can be used to heat the soil either in situ or ex situ. Heat is injected either through surface layers or through vertical or horizontal wells in which thermal bars are placed. The heat is applied to the soil so that heat transfers by radiation and convection to be effective in the whole volume of soil. Solids are based on molecular movements in the soil through heat transmission by convection.

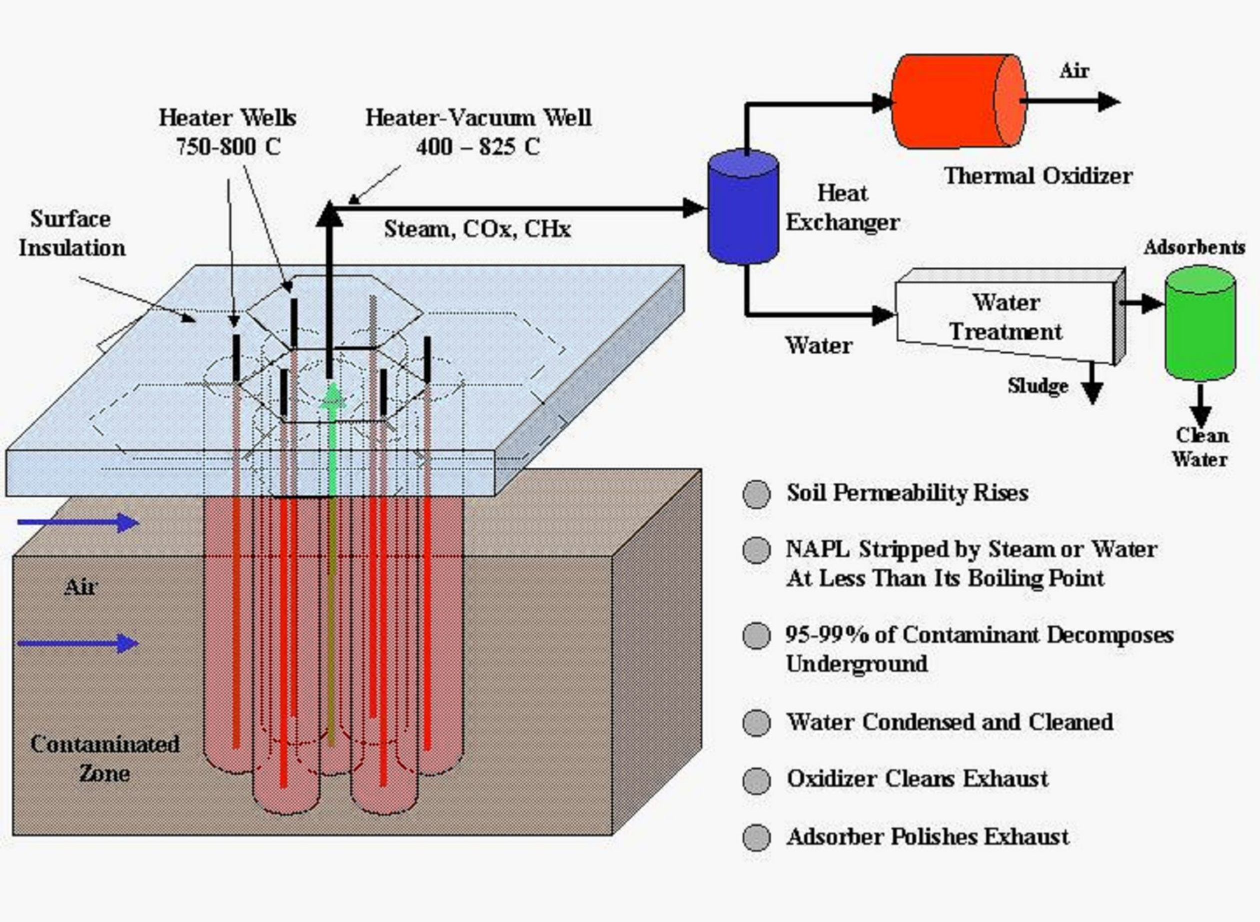

Figure 6. In situ thermal desorption (www.terratherm.com).

Results and Discussion. In situ thermal desorption is well suited for contamination with volatile or semi-volatile (VOC and SVOC) hydrocarbons, with PAHs, PCBs, dioxins/furans, with pesticides or other organic compounds.

The process was developed through a joint research program by TerraTherm and RT Environmental and General Electric/USA. The technology was demonstrated on different sites, achieving satisfactory results every time. TerraTherm ISTD technology treatment costs are estimated between $ 100 and $ 300 per ton of soil (Fig. 7).

In Portland Indiana site there were installed 130 wells. In these heat sinks the thermal bars were mounted at a distance of 7.5 m apart.

After the remediation process was completed, the wells were removed and soil restoration began on the site by increasing the vegetation naturally. After a year, the site has been completely restored (Stegemeier & Vinegar 2001).

Figure 7. In situ thermal desorption in Portland, Indiana (Stegemeier & Vinegar 2001).

Advantages:

- large soil treatment capacity, about 25 tonnes per hour;
- competitive costs for large volumes of soil, 30-70 $/ton of contaminated soil;
- soil can be treated on the spot without the risk of polluting other regions through transport;
- 98-99% high yields;
- it may be applied to areas under buildings or in places inaccessible to other machines.

Disadvantages:

- more time required for the soil treatment (2 days to 10 days);
- more facilities (facilities for vacuum and recovery of gas resulting from the process);
- in-situ thermal desorption can be applied on smaller areas of land unlike ex situ thermal desorption;
- it's only suitable for permeable sandy soils.

Conclusions. The effectiveness of the process was demonstrated in the case of soils contaminated with volatile heavy metals (mercury), oil (petrol, diesel), pesticides and nitrate compounds.

Thermal desorption requires lower costs compared to other methods remediation by thermal ways (incineration) and soil humic materials are not destroyed by burning.

Following the study we can conclude that the thermal desorption process has excellent results when the temperature applied to the contaminated soil and the duration of keeping the soil inside the furnace are properly selected depending on the type of pollutant found in the soil.

Optimum conditions for thermal desorption both in situ and ex situ are:

- ➢ temperature range that soil must reach for pollutants to volatilize and come off the soil matrix;
- ➢ soil moisture (if the soil contains more water it must be subjected to a dehydration before being placed in the desorption unit);
- ➢ type of treated pollutant;
- ➢ soil residence time inside the oven so that the efficiency is higher;

- for removal of volatile organic compounds, the soil should consist, ideally, of a humidity of 10-15%, since water vapors can entrain to some volatile organic compounds.

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