IN-PILE THERMAL DESORPTION OF DIOXIN CONTAMINATED SOIL AND SEDIMENT

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Abstract
Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs, or more simply, dioxins) are known human carcinogens. Dioxins are formed as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as forest fires. There have been many incidents of dioxin pollution resulting from industrial emissions and accidents; the earliest known incidents having occurred in the mid-18th century. Releases of dioxins related to industrial activity are known to have occurred in many countries.

Environmental restoration of dioxin-impacted sites has typically involved removal of impacted soils ands sediments, with either containment in a chemical disposal facility or incineration. Dioxins decompose at temperature ranges as low as 300 to 400°C in oxygen-deficient conditions.[1] The authors are in the process of evaluating a number of sites for the application of TerraTherm's In-Pile Thermal Desorption (IPTD) process as a means of performing thorough onsite thermal desorption and decomposition of dioxins. The benefits of on site treatment are no off-site transport costs, elimination of potential vehicular accidents associated with offsite transport and disposal, no long term liability, and unlimited onsite use of the impacted soils and/or sediment after treatment.

TerraTherm's design options include the use of a series of treatment piles or treatment cells, the latter of which each have a capacity of approximately 600 m^3, with a treatment time of 40 - 45 days. For treatment of PCDD/F-contaminated soil or sediment, the treatment piles or cells are heated under negative pressure to a minimum target temperature of 325°C. Multiple treatment piles or cells allow for the sequencing of treatment such that some are in operation while others are being constructed and yet others are in a cool-down mode / being sampled to confirm cleanup. Thus equipment and labor resources can be shared, allowing costs to be optimized.

Introduction

Polychlorinated dibenzodioxins and furans (PCDD/Fs), are commonly referred to as dioxins for simplicity in scientific publications because every PCDD molecule contains a dioxin skeletal structure. The word "dioxins" may also refer to a similar but unrelated compound, the polychlorinated dibenzofurans (PCDFs) of like environmental importance. Typically, the *p*-dioxin skeleton is at the core of a PCDD molecule, giving the molecule a dibenzo-*p*-dioxin two-ring system. Members of the PCDD/F family have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and human carcinogens frequently associated with soft-tissue sarcoma, non-Hodgkin's lymphoma, Hodgkin's disease and chronic lymphocytic leukemia.

There have been many incidents of dioxin pollution resulting from industrial emissions and accidents; the earliest such incidents being in the mid-18th century during the Industrial Revolution. Industrial sources common in the 20th century included manufacture of organochlorine chemicals, including polychlorinated biphenyls (PCBs), pesticides such as pentachlorophenol (PCP), dieldrin and chlordane, and herbicides/defoliants such as Agent Orange (2,4,5-T). Dioxin was a by-product of the manufacture of these compounds, and therefore tends to be found at sites where these compounds were manufactured, used or disposed. According to the most recent US EPA data, the major current sources of dioxins are:

- Coal fired utilities
- Municipal waste incinerators

- Metal smelting
- Diesel trucks
- Land application of sewage sludge
- Burning treated wood
- Trash burn barrels

These sources combined account for nearly 80% of current dioxin emissions.

The ISTD/IPTD Process

Thermal conductive heating (TCH) refers to the application of heat to the subsurface through conductive heat transfer. The source of heat is typically from thermal elements, which can be oriented both vertically and horizontally. TCH in combination with application of negative pressure (vacuum), as practiced by TerraTherm, Inc. is given the commercial name of In Situ Thermal Desorption (ISTD), also referred to as In Situ Thermal Destruction. ISTD can be used to remediate soils contaminated with a wide range of organic compounds. When applied ex situ for treatment of excavated soil or sediment, this technology is termed In-Pile Thermal Desorption (IPTD). ISTD and IPTD are protected by over 25 U.S. Patents, numerous international patents and Patents Pending. IPTD in particular is covered by one or more of the following U.S. Patents: 6,881,009; 7,004,678; and 7,534,926.

Figure 1 shows vapor pressures versus temperatures for a variety of environmental contaminants and in situ thermal remediation technologies. Because heat and vacuum are applied simultaneously over a period of time, compounds having relatively low vapor pressures at ambient temperatures can be thoroughly removed or destroyed in situ (e.g., by pyrolysis) using this technology. TCH is the only commonly available heating method capable of achieving soil / sediment temperatures well above the boiling point of water, which are necessary for treatment of Persistent Organic Pollutants (POPs) such as PCBs and PCDD/Fs.

Heat and vacuum are applied simultaneously to the target media with an array of vertical or horizontal heater elements. For the ISTD / IPTD technology, each heater contains a heating element (typically electrically powered resistance heaters), with an operating temperature of approximately ~750 to 800°C. As the soil is heated, volatile, semi-volatile and non-volatile organic contaminants in the soil are vaporized and/or destroyed by a number of mechanisms, including evaporation, steam distillation, boiling, oxidation and pyrolysis (chemical decomposition in the absence of oxygen).

The vaporized water and contaminants, as well as some volatilized inorganic compounds, are drawn counter-current to the heat flow into the vacuum extraction wells (termed "heater-vacuum" wells). Figure 2 provides a picture of a heating element that is encased in the heater well and the heater wellhead that contains the electrical connection within an enclosure (wellhead box). The same features apply to horizontally or vertically-oriented heaters.

Heat flows through the soil from the heating elements primarily by thermal conduction. As illustrated in Figure 3 the target temperature is the temperature that is maintained between the heater wells; the temperature immediately surrounding the heating wells is illustrated to range between 300 to 400°C, but can be as high as 500 to 700°C. With the soils under vacuum, desorbed contaminants are drawn through the higher temperature zones immediately surrounding the heater-vacuum wells, where in-situ destruction reactions occur at high rates.[2]

As with ISTD, the IPTD process utilizes conductive heating and vapor recovery to remediate excavated soil and/or sediment contaminated with semi-volatile organic compounds (SVOCs), such as dioxins. Heat and vacuum are applied simultaneously to the treatment piles or cells with an array of horizontal heaters and vapor collectors.

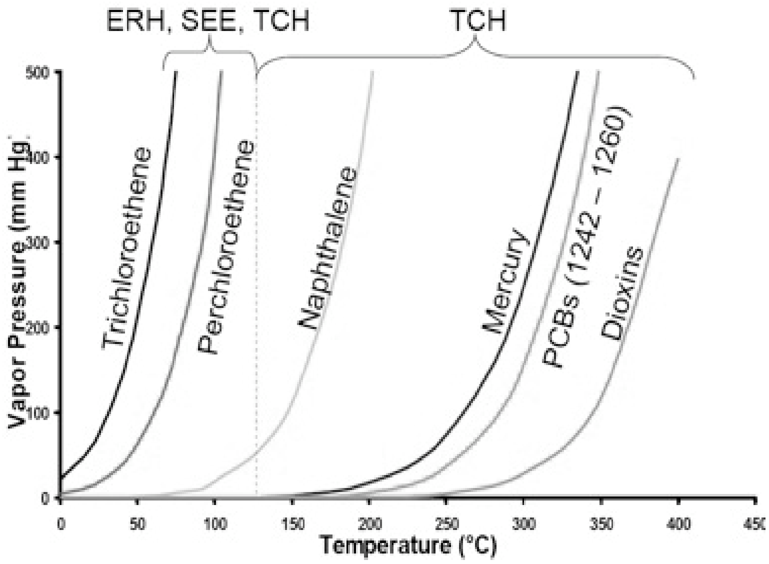

Figure 1: Vapor pressures versus temperatures and environmental contaminants that can be treated using commonly available in-situ thermal methods. ERH = electrical resistance heating; SEE = steam enhanced extraction; and TCH = thermal conductive heating.

In a typical IPTD installation for soils or sediments contaminated with high-boiling point semi-volatile organic compounds (SVOCs), such as dioxins, the coolest soil in between the heaters is heated to a target treatment temperature of 325°C. Experience has shown that due to the long residence time at temperature using this technology, achieving the boiling point of the contaminant of concern (COC) is not necessary to accomplish thorough desorption and treatment. Based on various field studies, regardless of the type of COC, most (e.g., >95-99% or more) of the SVOCs are destroyed as they pass through the superheated soil in proximity to the heater-vacuum wells, before they arrive at the extraction wells.[3,4]

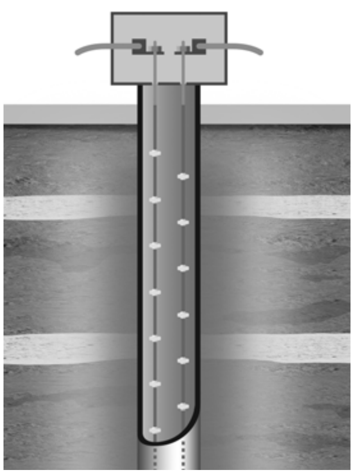

Figure 2: Heater element contained within a vertically-oriented heater well. Horizontally-oriented heater wells are similar.

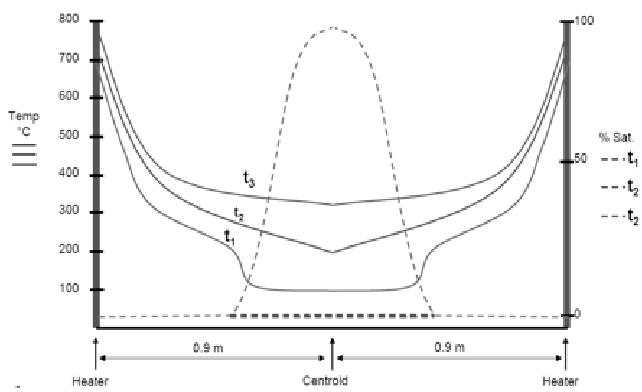

Figure 3: Temperature distribution between heater wells. The curves indicate the progression of heating up to the 325°C target temperature for dioxin-contaminated soil or sediment. *N.B.:* Time step 1 (t_1) depicts the heating process already underway, with locations between heater wells already up to the boiling point of water but still moist. Time step 3 (t_3) shows attainment of target treatment temperature at the centroid, with all water having been boiled off.

Materials and Methods

Typical IPTD design options include either treatment piles of various sizes (Figure 4) or treatment cells containing approximately 600 m^3 each (Figure 5). Multiple adjacent treatment piles or cells would be constructed and utilized simultaneously. Design features include:

- A base pad that is both vapor-and liquid-tight.
- A leachate collection system, such as with a collection pipe installed in a trough running down the center of each treatment pile or cell, or with a catch basin.
- Thermocouple ports installed through the surface cover and/or running laterally through the side walls at select locations to enable tracking of heating progress.
- In the case of treatment cells, rigid sidewalls, with insulating panels to reduce heat losses during treatment.
- Heater elements and vapor injection and extraction wells distributed throughout each treatment pile or cell.
- A soft insulating vapor cap used to contain fugitive emissions and allow for application of a net vacuum to each treatment pile or cell.
- Contaminants that have not been destroyed within the soil are removed from the produced vapor stream with the Air Quality Control (AQC) system. Repeated rounds of source testing have indicated that the off-gas emissions remained well below the required standard.

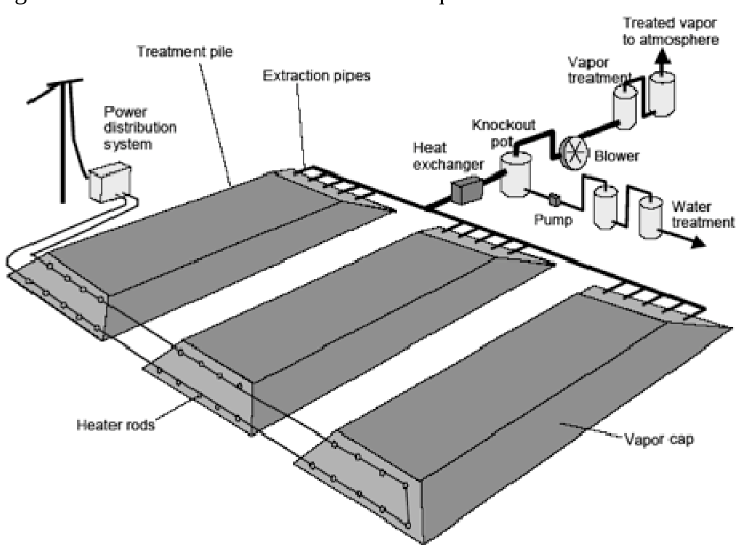

Figure 4: IPTD Schematic. Treatment pile configuration, showing ancillary electrical distribution gear, and one of several possibly Air Quality Control systems.

Results and Discussion

TerraTherm's proprietary ISTD / IPTD technology has been used successfully at 3 field-scale projects in the U.S. treating PCDD/Fs (Table 1), of which one was demonstration-scale (Missouri Electric Works Superfund Site, Cape Girardeau, MO) and included both ISTD and IPTD tests, and the remaining two projects were full-scale (US Navy, Centerville Beach, CA, and Southern California Edison, Alhambra, CA). Note that while mean pre-treatment PCDD/F concentrations were as high as 18,000 pg TEQ/g, mean post-treatment concentrations ranged from 3.2 to 110 pg TEQ/g, and were well below the typical remedial goal of 1000 pg TEQ/g.[5,6,7] All projects met the USEPA Toxic Substances Control Act (TSCA) standard of >99.9999% Destruction and Removal Efficiency (DRE).

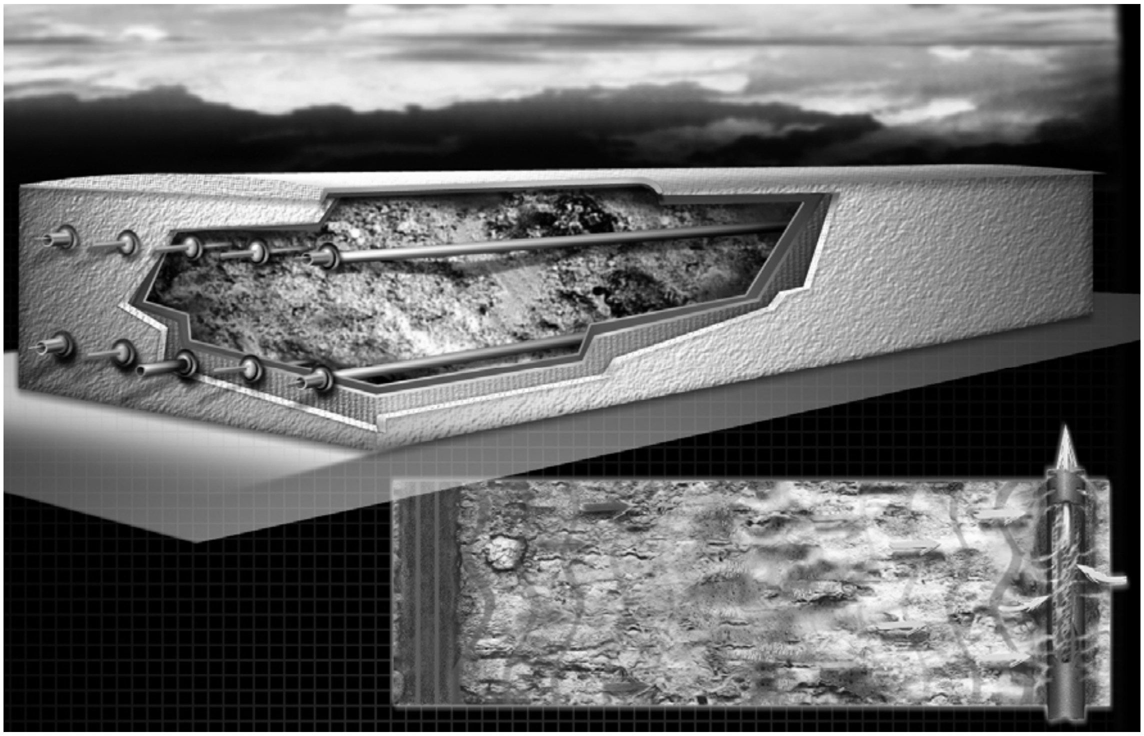

Figure 5: IPTD treatment cell configuration showing soil and heaters. Inset is a view looking down on the cell between a heater-only well on left and a heater-vacuum well on right, during heating and vapor extraction.

Table 1: Documented results of field-scale ISTD/IPTD treatment of dioxin-contaminated soil.[5,6,7]

Site	Treated Volume	Before treatment	After treatment	Source test
		Mean Soil Concentration	Mean Soil Concentration	Exhaust gas
	[m^3]	[pg-TEQ/g]	[pg-TEQ/g]	[pg-TEQ/Nm3]
Southern California Edison Alhambra Combined Facility AOC-2, Alhambra, CA USA	12,615	18,000	110	7.1
Missouri Electric Works Superfund Site, Cape Girardeau, MO USA	5.7	6,500	3.2	2.9
Former US Naval Facility Centerville Beach, Ferndale, CA USA	765	3,200	7.3	5.46

Remediation of dioxin-, furan- and PCB-contaminated soils and sediment has in the past been largely limited (depending on concentration) to excavation and disposal in chemical disposal facilities, permitted landfills or incineration. Regulatory agencies have been stipulating very low cleanup criteria, requiring in many cases high-temperature incineration, which is very expensive. When utilizing ISTD / IPTD technologies, by contrast, destruction of these compounds through thermal desorption and decomposition occurs at temperatures at or about 325°C, with treatment taking place over a typical period of 45 days. This results in better than 99% reduction in concentrations, which in turn can result in unlimited soil use after treatment, as was the case at the Southern California Edison, Alhambra, CA project, where regulators granted a No Further Action letter with unrestricted land use.[5]

There are a limited number of incineration facilities in North America, involving long distance trucking of contaminated soils and sediments for treatment. According to the Center for Transportation Research and Education, at Iowa State University, the U.S. national trucking accident rate is 2.04/million miles driven. Long distance trucking of hundreds of truckloads of contaminated soils results in high probabilities of vehicular accidents involving toxic payloads.

Long distance trucking of soils and sediment for incineration also increases the carbon footprint for the project and as noted above the burning of diesel fuel can also result in the formation of dioxin. The IPTD technology represents a cost-competitive means of remediation of dioxin-contaminated sites without the adverse impacts associated with current approaches.

Acknowledgement
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