In-Situ Thermal Destruction (ISTD)

Name of Process:

In-Situ Thermal Destruction (ISTD)

Vendor:

TerraTherm, Inc

Web site: http://www.terratherm.com

Applicable Pesticides and related POPs wastes:

ISTD is applicable to all organic pesticides.

Status:

Since 1997, ISTD has treated a wide range of chlorinated organic compounds, including polychlorinated biphenyls (PCBs); chlorinated solvents (e.g., trichloroethene [TCE], tetrachloroethene [PCE]); mono- di- and trichlorobenzenes; and polychlorinated dibenzodioxins and furans (PCDD/Fs).

USEPA has granted TerraTherm's ISTD a draft Nationwide Toxic Substances Control Act (TSCA) Permit.

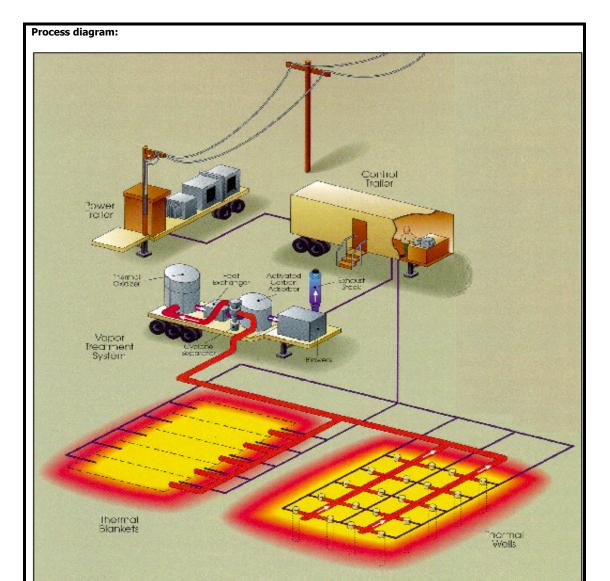
A famous project where ISTD has been applied is the Rocky Mountain Arsenal (RMA) Commerce City, CO, USA. This is one of the U.S. Department of Defense's most complex CERCLA sites with its socalled Hex Pit. The Hex Pit Unit contains buried pesticide wastes derived from post-World War II conversion of chemical weapons facilities to commercial pesticide manufacturing. The Hex Pit was the only in-situ destruction of hazardous material attempted at RMA and it was conducted under the scrutiny of the USEPA's Superfund Innovative Technology Evaluation (SITE) program.

Technology description:

In-Situ Thermal Destruction (ISTD) is a soil remediation process in which heat and vacuum are applied simultaneously to subsurface soils, either with an array of vertical heater/vacuum wells, or, less commonly, with surface heater blankets. No excavation is necessary. Thermal conduction accounts for the majority of heat flow from the high temperature (~800° C) heaters. As soil is heated, volatile and semi-volatile contaminants in the soil are vaporized and treated by a number of mechanisms, including: (1) evaporation into the subsurface air stream induced by application of vacuum, (2) steam distillation into the water vapor stream, (3) boiling, (4) oxidation, and (5) pyrolysis. The vaporized water, contaminants, and natural organic compounds are drawn by the vacuum in a counter-current direction to the heat flow into the vacuum source at the thermal wells or blankets.

Compared to fluid injection processes, conductive heat injection is very uniform in its vertical and horizontal movement. Furthermore, transport of the vaporized contaminants is enhanced by the creation of permeability that results from drying and shrinking of the soil. Flow paths are created even in tight silt and clay layers, which allow escape and capture of the vaporized contaminants. The combined effectiveness of both heat and vapor flow yields nearly 100% sweep efficiency. In addition, very high displacement efficiency (approaching 100%) can be reached in the heated soil. This occurs because the soil can, if needed, be heated to high temperatures (>500°C) for prolonged times (many days).

Field project experience has confirmed that a combination of high temperature and long times result in extremely high overall removal of even the high boiling point contaminants from the soil. Data indicate that 95 to 99% or more of the contaminant mass is destroyed in situ, as the vaporized contaminants pass through superheated soil close to the heatervacuum wells. In practice, produced vapors are treated with an air pollution control (APC) system to remove any vaporized contaminants that have not been destroyed in situ.



- --> Electrical distribution trailer with utility pole power drop is at top left, and Control trailer with continuous emission monitoring system (CEMS) is at top right.
- --> Air Quality Control Trailer (at center) includes unit processes for treatment of Semi-Volatile Organic Compounds, such as pesticides, PCBs and dioxins. These include particle separator, thermal oxidizer, air-to-air heat exchanger, carbon and acid-gas scrubber canisters, redundant discharge blowers, stack, and control cabinets.
- --> Āir Quality Control for treatment of Volatile Organic Compounds such as chlorinated solvents generally consists of fewer unit processes (e.g., carbon adsorption only).

Performance:

Treatment efficiency:

At the Missouri Electric Works (MEW) Superfund Site, Cape Girardeau, Missouri USA, ISTD treatment to soil temperatures of $> 480^{\circ}\text{C}$ over a period of 42 days was demonstrated to achieve the following results: pre-treatment PCB concentrations averaged 782 mg/kg (n=92), with maximum concentration of 20,000 mg/kg; and post-treatment PCB concentrations averaged <0.033 mg/kg (n=83) [4]. The combination of ISTD and an off-gas treatment system consisting of flameless thermal oxidizer, heat exchanger, and adsorption on granular activated carbon demonstrated achievement of >99.999999% Destruction and Removal Efficiency (DRE) and served as the basis for the granting by USEPA of a draft Nationwide Toxic Substances Control Act (TSCA) Permit. Similar treatment results at other sites have demonstrated that ISTD typically reduces even high concentrations of organic contaminants in soil to non-detect concentrations.

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At a Demonstration project for the California EPA, at the Former Mare Island U.S. Naval Shipyard, from September through December 1997, PCB-contaminated soils were treated with ISTD, and a DRE for PCB (Aroclor 1260) in excess of 99.9999% was reached. All post-treatment samples had no-detectable PCB concentrations at a quantitation limit of 10ug/kg) [11], [15].

At the Tanapag Village Site, Saipan, NMI, 1000 cubic yards of PCB-impacted soil were treated using an ex-situ version of ISTD to 10 ppm or less. Concentrations had been represented to average 200 ppm, but in fact concentrations averaged 500 ppm, (Arochlor 1254 and 1260) and individual batches were 10 000 ppm.) [12], [15].

From September through December 1998, ISTD was utilized to treat a PCB Spill Area at the U.S. Naval Facility Centerville Beach (NFCB), Ferndale, CA containing around 1000 cubic yards of PCB-contaminated soils under/adjacent to a former transformer /diesel generator building. Target treatment area achieved the remedial objectives for all samples (Average PCB concentration of 1 ppm or lower; Dioxins and Furans: Total 2,3,7,8 –TCDD TEQ <1.0 ppb) [13], [15].

Rocky Mountain Arsenal (RMA) Commerce City, CO, USA is one of the U.S. Department of Defense's most complex CERCLA sites. The Hex Pit unit contains buried pesticide wastes derived from post-World War II conversion of chemical weapons facilities to commercial pesticide manufacturing. The vast majority of the RMA site is being remediated by relocating contaminated material to an on-site landfill and capping the lower level contamination in place. The Hex Pit was the only in-situ destruction of hazardous material attempted at RMA and it was conducted under the scrutiny of the USEPA's Superfund Innovative Technology Evaluation (SITE) program [16].

The RMA ISTD pesticide project mentioned above was curtailed due to acid corrosion of stainless steel piping after 12 days of heating. The vendor believes this material failure was a result of hydrochloric acid corrosion due to organochlorine pesticide tars being forced into the annuli of our heater-vacuum wells prior to heating as a result of horizontal well drilling activities carried out by others beneath the Hex Pit. Such drilling occurred beneath the bottom of the Hex Pit following installation of the ISTD well field, but prior to ISTD heating. The evidence of this deleterious impact was: (1) the appearance of frac-outs of drilling fluid that emerged under the ISTD well field surface cover during horizontal drilling, and (2) the subsequent finding (after ISTD heating and shut-down) that nearly all of the most severely-corroded heater-vacuum wells were located directly above the horizontal well that produced the most frac-out events. It is recommended that future applications of ISTD in pesticide waste pits would need to begin with an ISTD pilot test to confirm the compatibility of the piping metallurgy with the pesticide waste materials.

ISTD Performance relative to Dioxins [14]

The vendor has been performing very much work in studying this issue and due to this reason has been included quite extensively in this Fact Sheet [14]:

ISTD is fundamentally different than conventional ex-site treatment technologies like low- and high temperature thermal desorption and incineration.

ISTD does not employ flame-based thermal combustion to remove and destroy contaminants in-situ or in the treatment of the off-gas and therefore does not create the conditions typically required for the creation of dioxins and furans as enumerated below.

EVIDENCE THAT ISTD DOES NOT CREATE, OR RELEASE DIOXINS AND FURANS BELOW GROUND

Field-scale ISTD projects have demonstrated that dioxins or furans remaining after thermally treating PCB-contaminated soils were less than the average concentration in uncontaminated soils in North America (1, 6) (i.e., post-ISTD treatment soil samples were below "background" concentrations for North American soils). There has been no evidence from these projects that dioxins or furans were formed in or around the soil of the thermal treatment zone during ISTD. Table 1 summarizes the results of soil sampling and analyses for both PCBs and dioxins before and after ISTD at the Missouri Electric Works (MEW) Superfund Site, Cape Girardeau, MO (7) and at the U.S. Naval Facility Centerville Beach (NFCB), Ferndale, CA (8). The post-treatment soil concentrations are clearly much lower than the pre-treatment concentrations. The previously cited data for a treatability study of PAH- and dioxin-contaminated soil from the Southern California Edison (SCE) Former Pole Yard, Alhambra, CA (4) is included in Table 1 for comparison.

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Table 1. Pre- and post-treatment PCB and dioxin soil concentrations measured during ISTD projects.

LOCATION	MEAN AIR FLOW RATE (SCMM ¹)	MEAN OXIDIZER BED TEMPERATURE (°C)	MEAN EMISSION RATE (g TEQ/hr)	MEAN STACK GAS CONCENTRATION ² (ng TEQ/dscm)	
S. Glens Falls, NY Thermal Blanket Demo (PCBs) ²	42.5	960	1.2 x 10 ⁻⁶⁰	0.004	
Cape Girardeau, MO Thermal Well Demo (PCBs) ⁴	2.1	1027	3.47 x 10 ⁻¹⁰	0.00291	
Cape Girardeau, MO Thermal Blanket Demo (PCBs) ⁵	2.6	1027	4.51 x 10 ⁻¹¹	0.000289	
Centerville Beach, CA Thermal Well Demo (PCBs) ⁶	4.9	927	1.84 x 10 ⁻⁰⁹	0.00547	

¹ SCMM = standard cubic meters per minute

EVIDENCE THAT ISTD DOES NOT CREATE, OR RELEASE DIOXINS AND FURANS ABOVEGROUND

ISTD systems are designed to prevent emission of dioxins or furans or their formation in aboveground treatment units. The protective design elements include: (a) insertion heaters to preheat the vapor collection manifolds, thereby preventing condensation of off-gases during conveyance from the well field to the treatment unit; (b) a flameless thermal oxidizer (FTO) operated at 1700F, that provides a large reaction chamber at very uniform high temperature (in contrast to a locally very hot flame/burner in an incinerator and to the lower temperatures of catalytic oxidizers), and a resulting oxidation zone with sufficient supply of free radicals thereby ensuring a high destruction and removal efficiency for organic contaminants including PCDD/Fs and PCDD/F precursors (e.g., 99.99% DRE within the FTO) and the prevention of the formation of PICs; (c) an air-to-air heat

exchanger to reduce the temperature of the off-gases at the oxidizer outlet within a fraction of a second to \sim 250F, well below the dioxin formation range; and, (d) polishing of off-gas with granular activated carbon (GAC) adsorbers prior to the discharge stack. The combined destruction and removal efficiency of the in-situ processes and the off-gas treatment achieved using ISTD for the treatment of PCB sites has been demonstrated to be >99.999999% (Table 2).

Table 2. Dioxin stack emissions measured during ISTD projects. Air quality control systems consisted of a flameless thermal oxidizer, heat exchanger, and granular activated carbon.

LOCATION	MEAN PRE-TREATMENT PCB SOIL CONCENTRATION (µg PCB/kg)	MEAN POST- TREATMENT PCB SOIL CONCENTRATION (µg PCB/kg)	MEAN PRE-TREATMENT DIOXIN SOIL CONCENTRATION (µg TEQ/kg)	MEAN POST- TREATMENT DIOXIN SOIL CONCENTRATION' (µg TEQ/kg)
Cape Girardeau, MO ² Thermal Well Demo (PCBs)	649,000 (n = 111)	22 ³ (n = 101)	6.54	0.0032 (n = 4)
Centerville Beach, CA Thermal Well Demo (PCBs) ⁵	302,000 (n = 6)	85 ⁶ (n = 16)	1.7 (n = 2)	0.011 (n = 10)
Alhambra, CA Treatability Study (PAHs) ⁷	N/A	N/A	1.23 (n = 1)	0.061 (n = 6)

¹ For comparison, background level in uncontaminated North American soils = 0.0079 μg TEQ/kg, per Reference (6)

² ng TEQ/dscm = nanograms 2,3,7,8-Tetrachlorodibenzodioxin Toxic Equivalency per dry standard cubic meter

Reference (9), Tables 3A and 9. Stack sampling was performed isokinetically by Air Pollution Characterization and Control Ltd., Tolland, CT with PCDD/PCDF analyses (EPA Method 23) by Triangle Laboratories, Durham, NC.

⁴ Reference (7) Stack sampling was performed isokinetically by ENSR Corporation, Houston, TX with PCDD/PCDF analyses (EPA Method 23) by Triangle Laboratories, Durham, NC.

⁵ Reference (10) Stack sampling was performed isokinetically by ENSR Corporation, Houston, TX with PCDD/PCDF analyses (EPA Method 23) by Triangle Laboratories, Durham, NC.

analyses (EPA Method 23) by Triangle Laboratories, Durham, NC.

Reference (8) Stack sampling was performed isokinetically by Arcadis Geraghty & Miller, Mountain View, CA with PCDD/PCDF analyses (EPA Method 23) by Alta Analytical Laboratories, El Dorado Hills, CA.

² Reference (7) Soil sampling was performed by Philip Environmental, Columbia, IL with PCDD/F analyses (EPA Method 8280) by Triangle Laboratories, Durham, NC.

Of 101 samples analyzed, 94 samples were below the detection limit of 33 µg PCB/kg. Mean was calculated by taking % of the detection limit for each sample below detection limit.

Estimated value, based on an assumption that dioxins and furans are typically present in PCB Arcclor mixtures at a concentration of 1 part in 100,000.

⁵ Reference (8) Soil sampling was performed by Radian and TTEMi, Rancho Cordova, CA with PCDD/F analyses (EPA Method 8280A) by Triangle Laboratories, Durham, NC.
⁶ Of 16 samples analyzed, all were below the detection limit of 170 μg PCB/kg. Mean was calculated by taking ½ of the

Of 16 samples analyzed, all were below the detection limit of 170 µg PCB/kg. Mean was calculated by taking ½ of the detection limit.

⁷ Reference (4) Pretreatment concentration elevated due in part to use of low resolution version of EPA Method 8280, which has higher detection limits.

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SUMMARY

In summary, there is no evidence to support the contention that ISTD results in the formation or release of dioxins or furans, either in the treated soils or in the off-gas. Quite to the contrary, the evidence indicates that ISTD applied to sites with high levels of chlorinated hydrocarbon contamination exceeded the soil cleanup objectives and reduced levels of PCDD/Fs in treated soils to near background levels, while achieving air emissions of PCDD/Fs well below mandated MACT standards.

Throughput:

ISTD, being an in-situ process, can be applied at a wide range of scales. Soil and waste volumes of 500 to 10,000 m³ or more can be remediated in a single, 2- to 3-month batch treatment. Larger sites can be treated in a series of batches, utilizing the same equipment from batch to batch.

Wastes/Residuals:

Unlike standard ex-situ thermal desorption processes, ISTD produces negligible quantities of waste products. No liquid waste streams are generated, and the off-gas treatment has been demonstrated to achieve over 99.999999% Destruction and Removal Efficiency (DRE).

Reliability:

ISTD has been implemented at many sites without any U.S. Occupational Safety and Health Administration (OSHA) recordables or lost-time accidents to date. The reliability of ISTD at the field scale for pesticide remediation has not yet been confirmed.

Limitations:

Treatment of organo-pesticides using ISTD requires attainment of soil/waste temperatures above the boiling point of water; thus, excessive recharge of groundwater into the treatment zone may prevent water from being boiled off cost-effectively and retard achievement of target temperatures. Control of groundwater recharge into the thermal treatment zone, using groundwater pumping or hydraulic barriers such as steel sheeting, slurry walls, freeze walls, etc. may therefore be necessary in such cases. Heating of highly concentrated, heavily chlorinated pesticide liquids can result in hydrolysis with resulting production of highly corrosive hydrochloric acid (HCl). However, use of appropriate neutralization materials in the sand pack around the heater-vacuum wells, and/or more corrosion-resistant metallurgy may be able to minimize these effects and protect against HCl corrosion.

Transportability:

ISTD can be implemented in virtually any location with access to adequate grid-based or portable power supplies. The power required depends largely on how much water is present in the soil, the target treatment temperature and the rate at which groundwater seeps into the treatment zone.

Conclusion:

The status of the ISTD process for treatment of pesticides is that several successful bench-scale treatability studies have been completed, but that the process has not yet been demonstrated on pesticides at the field scale. However, five successful field-scale applications of ISTD for PCBs, plus others for chlorinated solvents and petroleum hydrocarbons, along with the similarities between pesticides and those compounds indicates that the technology is well-suited for remediation of pesticides. The maturity of the ISTD process can be concluded also at the fact that at present TerraTherm is under contract at three major sites in The United States and is in the process of securing two other projects.

Detailed information:

See Data in Annexes

Full Scale treatment examples:

At present TerraTherm is under contract at three major sites in The United States and is in the process of securing two other projects. Also, TerraTherm holds world-wide rights to license and implement ISTD.

- ISTD Remediation of polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), and Dioxins, 10,500 m³ of silty-sand soil up to 30 m below ground surface (BGS), extremely low (detection limit) clean-up goals, May 2002 December 2003
- Confidential Client, Ohio Active manufacturing facility, ISTD Remediation of chlorinated volatile organic compounds (CVOCs), 7,700 m³ of low permeability clay, clean-up goal: 1 mg/kg TCE, July 2002 – June 2003
- Confidential Client, California Former manufacturing facility, thermal enhancement of existing multiphase extraction (MPE), 11,400 m³ of silty-clay soil, above and below water table, clean-up goal: 1 mg/kg dichloroethene (DCE), September 2002 – August 2003

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*Note: This NATO/CCMS fellowship report does not certify any particular technology, but tries to summarise the state of the art of the concerned technology on the basis of data delivered by the company or other source, which have been made available to the author and refers the reader to original documents for further evaluation. Without the efforts of the Technology supplier it would not have been possible to set up this fact sheet.

** Note: The text for this report is verified by the Technology supplier on 11. December 2002

Patent Notice:

Covered by one or more of the following U.S. patents: 4,984,594, 5,076,727, 5,114,497, 5,169,263, 5,190,405, 5,193,934, 5,209,604, 5,221,827, 5,229,583, 5,233,164, 5,244,310, 5,271,693, 5,318,116, 5,553,189, 5,656,239, 5,660,500, 5,674,424, 5,997,214, 6,102,622 and 6,419,423. Additional Patents Pending both within the U.S. and internationally. All rights reserved by the University of Texas at Austin, Shell Oil Co., and TerraTherm, Inc.

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