



TerraTherm, Inc.

# Remediating Subsurface Mercury Contamination using TerraTherm's ISTD Technology

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## **Executive Summary**

TerraTherm, Inc. (TerraTherm) has adapted its In Situ Thermal Desorption (also known as In Situ Thermal Destruction) (ISTD) technology for remediation of sites containing subsurface mercury. Substantial amounts of mercury are found at industrial sites historically involved in chlor-alkali manufacturing using mercury cells, in addition to many DOE applications that utilized elemental mercury during chemical processing operations.

This analysis will discuss the basic physical and chemical properties of elemental mercury that tailor the remediation requirements to achieve comprehensive removal of subsurface contamination. Subsequently, the modifications incorporated into the standard TerraTherm component designs are discussed to facilitate the understanding of the strategy and course of a typical mercury remediation.

Readers that are not familiar with TerraTherm's ISTD technology are urged to visit [www.terratherm.com](http://www.terratherm.com) or contact TerraTherm's home office for additional information concerning the ISTD technology and its multiple successful commercial scale demonstrations to date.



## 1. Introduction to In-Situ Thermal Desorption

*In-Situ* Thermal Conduction Heating is a soil remediation process in which heat and vacuum are applied simultaneously to subsurface soils. Radiation heat transport dominates near the heaters, which are operated at 1400 to 1600° Fahrenheit; however, thermal conduction accounts for most of the heating within the soil.

As soil is heated, contaminants in the soil are vaporized or destroyed by a number of mechanisms, including (1) evaporation into the air stream, (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 direction countercurrent to the heat flow into the heater-vacuum wells.

Compared to fluid injection processes, the conductive heating process is very uniform in its vertical and horizontal sweep. Furthermore, transport of the vaporized contaminants is improved by the creation of permeability, which results from drying and shrinking of the soil. Flow paths are created even in tight silt and clay layers, allowing escape and capture of the vaporized contaminants. The combined effectiveness of both heat and vapor flow yields nearly 100% sweep efficiency, leaving no area untreated.

Furthermore, the contaminants in the heated soil are almost completely removed, with a displacement efficiency approaching 100%. This occurs because the entire treatment zone may be heated to high temperatures (in some cases, approaching 1000°F) for many days. Laboratory treatability studies and field project experience have confirmed that the combination of high temperature and long time results in extremely high overall removal efficiency of even the high boiling point contaminants.

Owned by the University of Texas at Austin (U.S. rights) and by Shell Oil Company (international rights), and licensed exclusively to TerraTherm, ISTD is an innovative technology that involves simultaneously applying heat and vacuum to the soil to clean it up in place, without excavation. Multiple field scale demonstrations have shown that ISTD destroys most (~95 to 99% or more) of the contaminants in the ground<sup>1</sup>, and removes the rest for aboveground treatment.

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<sup>1</sup> Stegemeier, G.L., and Vinegar, H.J. 2001. "Thermal Conduction Heating for In-Situ Thermal Desorption of Soils." Ch. 4.6, pp. 1-37. In: Chang H. Oh (ed.), *Hazardous and Radioactive Waste Treatment Technologies Handbook*, CRC Press, Boca Raton, FL.



## 2. Introduction to Mercury and its properties

Subsurface mercury (Hg) represents a substantial remediation challenge due to its unique chemical and physical properties. Those properties are briefly summarized below:

- 1) Stable element – not capable of chemically reacting to a less toxic form
- 2) Soluble in water at low part per billion levels – removed by Granular Activated Carbon (GAC)
- 3) Liquid density approximately 13 times that of water.
- 4) Molecular Weight of 200.61 – vapor roughly 7 times as dense as air
- 5) Atmospheric boiling point of 360°C (680°F)
- 6) Stable viscosity near 1 centipoise over a wide temperature range
- 7) Very low liquid heat capacity – 1/30<sup>th</sup> that of water
- 8) Low heat of vaporization – 125 Btu/lb at 360°C
- 9) Significant vapor pressure variation between ambient temperature and boiling point

The variation of vapor pressure is the unique physical property that dictates many of the features of the ISTD remediation of mercury contamination. Figure 1 on the next page shows the mole fraction of mercury in the vapor phase (in equilibrium with liquid mercury, which is often present in the contaminated subsurface soils) and the temperature and total system pressure. Note that the mole fraction of mercury in the vapor phase is shown on a logarithmic scale, with each colored band representing the range for one decade of mole fraction variation.

As can be seen in Figure 1, temperature is the dominant variable that dictates the mole fraction of mercury present in the vapor phase. The isotherms, which are the horizontal lines that diverge from the mole fraction colored bands as they go from left to right, show the minor impact of total system pressure over the range that can realistically be controlled in a subsurface remediation.

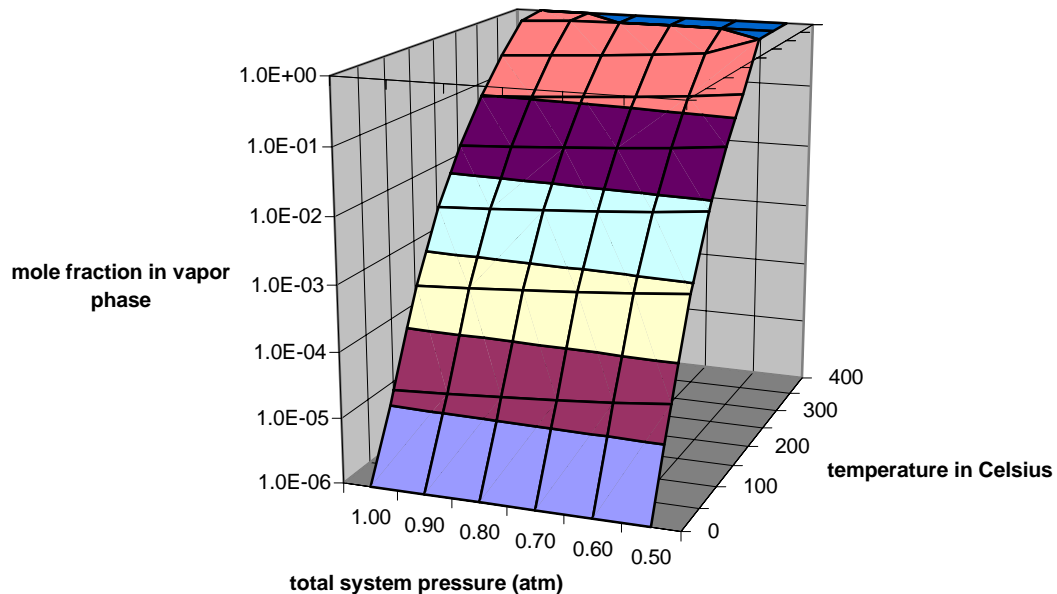
A few numerical values are worth identifying from Figure 1. The first is the equilibrium concentration of mercury in at ambient vapor, which is  $2.2 \times 10^{-6}$  mole fraction mercury, or 0.0017 torr at 25°C. This level corresponds to approximately 18 mg/m<sup>3</sup>, which is very close to the IDLH level of 28 mg/m<sup>3</sup>. However, as a removal mechanism, extraction with ambient air, as in Soil Vapor Extraction (SVE) will not remove an appreciable amount of mercury for a given volume of air (unless 0.5 mg/ft<sup>3</sup> of vapor is considered appreciable).

A second data point of interest is the mercury concentration at 100 Celsius, which might be encountered during steam stripping of a contaminated area. That value is  $3.7 \times 10^{-4}$  mole fraction, or 2.8 torr at 100°C. This level corresponds to



2.4 grams of mercury vapor per cubic meter, or 68 mg per cubic foot. While this level is significantly higher than the ambient mercury concentration, it is far from an expeditious removal mechanism.

Figure 1: Mercury vapor in equilibrium with liquid mercury



Finally, at 250°C, the vapor stream in equilibrium with liquid mercury contains 450 grams per cubic meter, or almost 13 grams of mercury per cubic foot, and is over 40% by weight mercury. It is achievement of temperatures above this threshold that allows ISTD to comprehensively remove the mercury from subsurface remediation sites.

### 3. ISTD Well Field Design and Layout

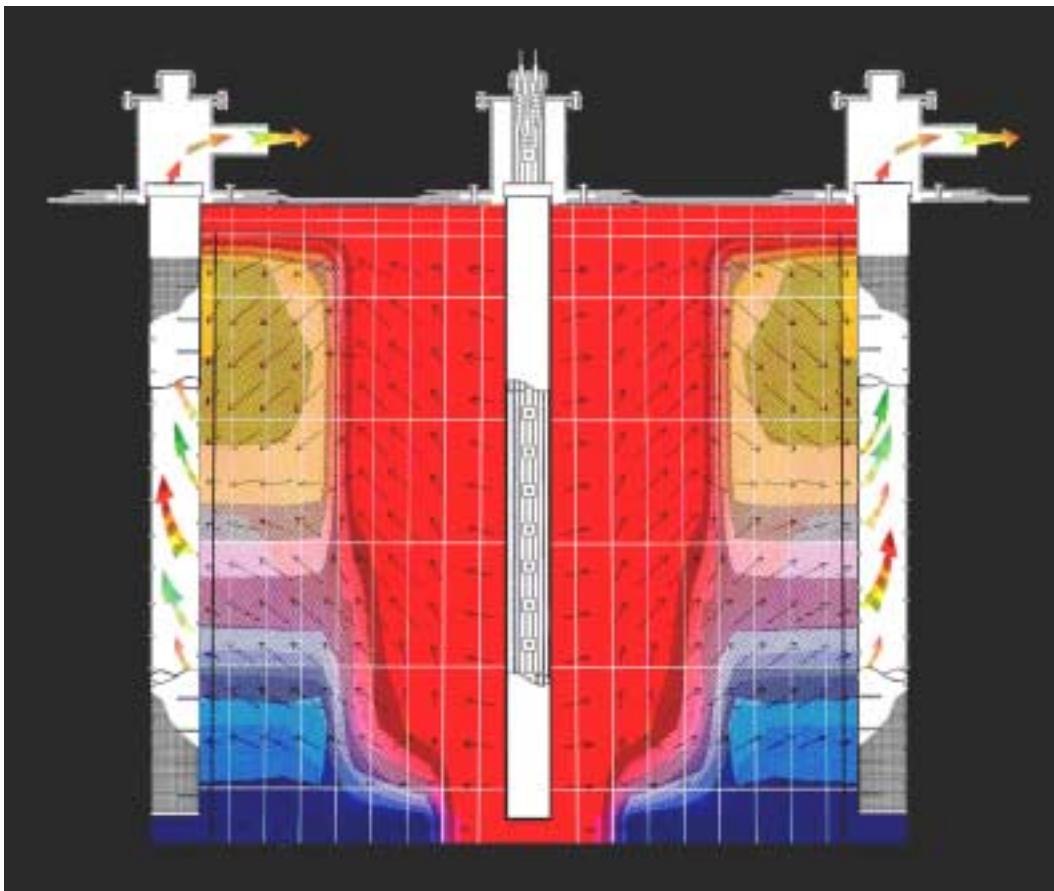
TerraTherm's ISTD technology is unique in that it creates very aggressive remediation conditions in-situ, thereby avoiding the effort and expense of removing the contaminated material, which would then require additional treatment or re-disposal.



The in-situ conditions are created by inserting combinations of heater-only wells and heater-vacuum wells throughout the target treatment zone. The thermal wells contain electrical resistance elements and operate at 1400 to 1600°F. The heaters transfer their heat principally by radiant heating to the inside of the well casing, with the subsequent heating of the adjacent soils principally by thermal conduction directly through the soils.

Around the heater-vacuum wells, vacuum is provided in addition to heating. The net effect is to establish a zone of vapor capture that extends from the heater-vacuum wells to the heater-only wells, as depicted in Figure 2. Figure 2 also shows the thermal gradient that develops as the well field heats up and which gradually diminishes as the average temperature within the well field increases and the radial heating from the heater-only wells reaches the heater-vacuum wells.

FIGURE 2: Heater-Vacuum Wells Capturing Volatiles from an Adjacent Heater-Only Well





There are many possible patterns for heater-vacuum and heater-only wells, with the exact configuration depending on soil and contamination properties. Figure 3 shows three possible combinations of heater and vacuum wells.

The patterns shown in Figure 3 differ in the number of heater-only wells supplied for each heater-vacuum well. The number of heater-only wells per heater-vacuum well is determined by noting, for example, that the 2:1 well pattern has each heater-only well shared by three heater-vacuum wells. Thus, each heater-only well is “shared” by three heater-only wells, and since there are six heater-only wells surrounding each heater-vacuum well, there is an equivalent of two heater-only wells per heater-vacuum well. In the 3:1 well pattern, each heater-only well is “shared” by two neighboring heater-only wells, and since there are again six heater-only wells surrounding each heater-vacuum well, there is an equivalent of three heater-only wells per heater-vacuum well. The 5:1 well pattern is achieved by combining the 2:1 and the 3:1 patterns.

There are several unique features of the ISTD well field as used to remediate a region of contaminated soil. The most significant feature is that the heat is distributed throughout the well field by the end of the remediation, without any zones left unheated. Furthermore, as the well field heats up past the boiling point of water, the soil is desiccated of moisture, which results in increased gas permeability, particularly in clayey soils. Thus, even clayey soils, or mixtures of sand and silt with clay that are initially impermeable will still develop relatively uniform vapor flow patterns after the removal of moisture.

The final and pivotal feature of the ISTD technology is the ability to heat the treatment zone significantly above the boiling point of water. As will be discussed, for the effective removal of mercury from contaminated soils, remediation technologies that cannot effectively elevate the soil matrix above the boiling point of water are not going to be able to remove residual amounts of mercury to acceptably low levels.

#### **4. Well Field Dynamics and Liquid Mercury Removal**

As the well field heats up, there is a very unusual sequence of events that occurs between the heater-only wells and the heater-vacuum wells. For most applications, the initial soil moisture provides sufficient steam generation at the heater wells to cause a “steam drive” that progressively travels from the heater-only wells to the adjacent heater-vacuum wells.

A “steam drive” is a thermal gradient that develops when a hot condensable vapor is convected into a cooler zone by a pressure gradient, such as the vapor flux that is created between the heater-only and heater-vacuum wells of the ISTD



well field. It is a common technique in secondary oil recovery, where steam is used to drive additional oil deposits towards producer wells.

The condensable vapor, typically steam, condenses upon reaching the cooler zone – which in turn heats the cooler zone by condensing. Over time, a wave front develops that has hot vapor on the backside and pushes a layer of cold liquid ahead of it. TerraTherm uses this technique to remove excess water from the well field by driving the interstitial water in the soil pore matrix toward the vacuum wells, where it can be removed as a liquid.

What is particularly interesting is the fate of other volatile compounds present in the soil as the steam wave front passes. As discussed by Udell<sup>2</sup>:

“5.1.3 Distillation in the Steam Zone. Depending on the volatility of a liquid-phase contaminant, it will either vaporize directly behind the steam condensation front or at a location far behind in the steam zone. .... In general, compounds with large vapor pressures or low residual saturations would be expected to be vaporized at a rate that is high enough that the hydrocarbon distillation wave velocity would be greater than the steam condensation front velocity. As such, the hydrocarbon liquid would appear to be displaced by the steam condensation front because any hydrocarbon left in the steam zone would vaporize, be convected to the steam condensation front, co-condense, and coalesce with any other hydrocarbon liquid in the vicinity. For hydrocarbon compounds with lower vapor pressures and/or high residual saturations, the distillation front would move through the soil with a velocity less than that of the steam condensation front. In that case, hydrocarbon liquids will remain in the steam zone and will be recovered through continuing steam distillation processes.”

Udell postulates that decane (bp 174°C) is the approximate demarcation for volatility that separates the compounds that volatilize with the steam condensation front and those compounds that lag behind the steam drive and require additional steaming to be driven through the soil matrix.

What is particularly interesting in the ISTD remediation of sites containing mercury is that mercury behaves as a high boiler, and lags behind the steam condensation front. Then, when the heating process has driven off all the residual soil moisture, the steam drive stops and the mercury remains behind in a treatment zone that has been stripped of volatiles and water.

Then, with additional heating, the well field temperatures rise significantly above the boiling point of water and produces a vapor stream that consists of inert vapor, due to the vacuum well flow, and condensable mercury vapor. It is believed that the mercury then forms a second condensing wave front, behaving

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<sup>2</sup> Kent S. Udell. *Heat and Mass Transfer in Clean-Up of Underground Toxic Wastes*, Chapter Six of the Annual Review of Heat Transfer, Volume 7, edited by Chang-Lin Tien, Begell House, Inc, New York (1996).



like the previous steam drive, but consisting of hot mercury vapor at the back pushing a colder zone of liquid mercury ahead of it toward the vacuum wells. For applications where significant liquid mercury is present in the soil matrix, it should be possible to capture and remove the bulk of the mercury as a liquid material at the heater-vacuum wells.

TerraTherm has modified its standard well designs to allow for the recovery of liquid mercury from subsurface remediation sites. As previously noted, excess groundwater is currently removed as a liquid from the heater-vacuum wells – typically by pumping the vacuum wells from above. However, it is not practical to pump mercury from above, since mercury will not pull to a height greater than 30 inches due to its density (hence the use of mercury in barometers).

Figure 4 shows the well details of the standard TerraTherm thermal wells and the modification adopted for removal of liquid mercury, which involves a down-well pump head with top mounted actuator (see Lift pump/Vacuum well detail). In practice, the appropriate well pattern (ref. Figure 3 and associated discussion) is installed and the heater-vacuum wells are activated briefly to desiccate the immediate region of the vacuum well. This has the effect of developing the heater-vacuum well for the uniform capture pattern from the heater well complex.

Upon establishing the desired vapor capture regime, the heater cores are removed from the heater-vacuum wells and the lift pump cores are installed into the vacuum wells. The heater-only wells are activated to provide the steam drive toward the vacuum wells, which can remove both liquid and vapor separately from the vacuum well boreholes. This configuration is operated until the volatiles, excess groundwater, residual steam and “mercury drive” are sequentially removed from the vacuum wells.

Depending on the level of mercury removal required, the heater-vacuum well cores can be replaced after the bulk of the liquid mercury is removed from the vacuum wells. At that point, the entire well field is heated and flushed with gas until the appropriate residual level of mercury remains in the target treatment zone. Because of the uniform heating throughout the well field and the high gas-filled porosity of the desiccated target treatment zone, coupled with the elevated temperatures possible with the ISTD technology (upwards of 1000°F with extended treatment times), de minimus residual levels of mercury can be achieved.

## **5. Off-Gas Treatment**

The off-gas treatment requirements for an ISTD treatment application are dictated by the contaminants in the target treatment zone and the proximity of the



nearest receptors. The ISTD treatment process itself creates a contained treatment cell with essentially complete capture of any volatiles and residuals removed from the subsurface. The resulting vapor and liquid streams are treated with standard proven treatment processes.

Figure 5 shows the “Typical ISTD Hydrocarbon Off Gas Treatment” process. TerraTherm has existing trailer-mounted treatment operations that are used and re-used at individual ISTD treatment sites, since the entire ISTD treatment process typically takes two to four months. The capacity of the currently available treatment trailers is from 125 scfm to 3000 scfm, which are capable of treating sites from a fraction of an acre to five or more acres at once.

The typical treatment process has a cyclone separator to remove dust and grit (generated when the well field desiccates), followed by a thermal oxidizer to destroy any volatiles present in the off-gases. In general, the predominant off-gas is methane, which results from the cracking and pyrolysis of hydrocarbons in the target treatment zone.

Following the thermal oxidizer is an air-to-air heat exchanger, which cools the thermal oxidizer flue gases to a temperature low enough for final polish treatment by granular activated carbon. The GAC serves to remove any trace toxics that may be formed in the oxidizer and acts as an emergency backup should the thermal oxidizer suddenly shut off (flame out, over-temperature cutout or loss of supplemental fuel supply).

Following the GAC polish, blowers provide the vacuum source for the entire well field and assure that any leaks in the treatment train infiltrate ambient air. Subsequently, the treated off-gas is exhausted to the atmosphere via a short stack.

For applications requiring just removal of mercury from the off-gases, the treatment scheme shown in the middle of Figure 5 is appropriate. The components of the typical treatment train have been reconfigured to allow the condensation of well field off-gases (when the steam drive breaks through to the heater-vacuum wells), followed by a second cyclone separator to remove the condensed liquid water and mercury. Subsequently, blowers provide the vacuum source and incrementally heat the uncondensed gases to avoid condensation in the GAC adsorbers that follow. For vapor phase mercury removal, a sulfur-impregnated granular activated carbon is used to provide comprehensive removal of mercury vapor.

As is often the case, contaminated industrial sites have multiple contaminants present. The bottom treatment scheme shown on Figure 5 can be used to treat off-gases that contain combinations of mercury vapor, hydrocarbon vapors and



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acid gases. For these applications, dry scrubber beds and a catalytic oxidizer augment the GAC treatment.

As expected, the specific size and extent of the sequence of off-gas treatment processes depends directly on the kinds and quantities of contamination found in the target treatment zone. However, TerraTherm has the advantage of being able to mix and match from in-house treatment unit operations to tailor an off-gas treatment train to the site remediation requirements.

## **6. Evaluating ISTD for Subsurface Mercury Removal**

TerraTherm welcomes the opportunity to evaluate the particulars of your mercury-contaminated site. The nature and extent of contamination, subsurface conditions, and the remedial goals / emission standards will largely determine the approach that is most cost-effective. Given the similarity between the boiling points of mercury and PCBs, and the proven performance of ISTD at five PCB-contaminated sites, we are confident that ISTD will prove to be equally capable of treating mercury-contaminated soils. Please contact us to initiate an evaluation for you.