

**APPENDIX A**

**TERRATHERM, INC. VENDOR REPORT: IN-SITU THERMAL DESTRUCTION (ISTD)  
AT ROCKY MOUNTAIN ARSENAL HEX PIT**

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Ralph S. Baker, James P. Galligan, and John M. Bierschenk  
(TerraTherm, Inc., Fitchburg, Massachusetts 01450, USA)

**EXECUTIVE SUMMARY**

Rocky Mountain Arsenal (RMA) is a former U.S. Dept. of Defense facility located in Commerce City, CO, just outside of Denver, that is in the process of undergoing remediation and conversion to one of the nation's largest urban wildlife refuges. A unit at RMA known as the Hex Pit contains buried organochlorine pesticide wastes, tars and residues derived from a period of post-World War II conversion of chemical weapons facilities to commercial pesticide manufacturing. Contaminants of Concern (COCs) identified at the Hex Pit included hexachlorocyclopentadiene (Hex), aldrin, dieldrin, endrin, isodrin and chlordane, compounds that all have high boiling points and are highly chlorinated. Delineation efforts identified approximately 2,550 cubic yards of impacted soil that required treatment.

Comprehensive treatability study and remedial design efforts led to the selection of TerraTherm's patented *In-Situ* Thermal Destruction (ISTD) technology, also known as *In-Situ* Thermal Desorption, for remediation of the Hex Pit. TerraTherm's ISTD technology utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil without excavation. As demonstrated in completed projects, the applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the vapor stream toward vacuum extraction wells. Because of the high inter-well temperatures possible (e.g., 300-600°C) and the fact that the vacuum extraction wells are also heater wells (operating at temperatures of 700-800°C), extracted vapors are exposed to high temperatures over a long residence time, and a significant percentage of the contaminant mass present in the subsurface is destroyed *in situ*. Contaminants not destroyed *in situ* are removed with the vapor stream and treated in an aboveground Air Quality Control (AQC) system consisting of a flameless thermal oxidizer, dry scrubbers and granular activated carbon. Based on treatability and design work, it was anticipated that >98% of the contaminant mass present would be destroyed in the heated soil at the Hex Pit, and that the remainder would be destroyed in the AQC system. In addition to oversight by federal, state and local regulatory agencies, the United States Environmental Protection Agency (USEPA) Superfund Innovative Technology Evaluation (SITE) program, as detailed in the accompanying report, scrutinized full-scale implementation of ISTD at the Hex Pit.

Upon the completion of the Hex Pit Treatability Study in February 2000, TerraTherm was selected to prepare the Remedial Design, which was prepared as four deliverables (30%, 95%, 95% Design Addendum, and 100%), the last of which was issued as the Final Design package in March 2001. TerraTherm was awarded the

remedial implementation contract in August 2001, initiated ISTD construction in September 2001, and completed construction and shakedown in February 2002.

On March 15, 2002, 12 days into the initial heating period, acidic corrosion of segments of the aboveground piping began to be observed, and TerraTherm recognized it as a potentially serious problem that, if allowed to continue, could have jeopardized the ability to collect and treat gases that were being generated from the subsurface. Therefore, TerraTherm shut down power to the thermal wells. Air sampling and analysis confirmed that none of the stipulated hourly rolling average air quality standards for off-gas emissions were exceeded. Site workers were protected from exposure to contaminants through appropriate use of Personal Protective Equipment throughout the subsequent assessment period.

With the concurrence of our client, Foster Wheeler Environmental Corporation (FWENC), which serves as the Program Management Contractor (PMC) at RMA; their client, the Remediation Venture Office (RVO) which represents the responsible parties at RMA; and the various Regulatory Agencies, TerraTherm commenced a comprehensive assessment of the damage to its piping system, the results of which were presented in a document entitled “Hex Pit Material Failure Assessment Report” [Assessment Report]<sup>1</sup>, and summarized herein.

TerraTherm found a total of three manifold stubs in the aboveground piping that failed due to acidic corrosion during operation. It appears that those failures were due to a combination of a higher than anticipated production of hydrochloric acid (HCl) coming out of the heater-vacuum wells, and, when exposed to the abnormally cold, subzero wind chill, in higher than anticipated heat losses from the short uninsulated piping legs located between the hot thermal wells and the heated manifolds. This enabled the temperature of the vapor stream (including steam, pesticides and HCl) at such portions of the piping to drop below the condensation points of the constituents. The resulting liquid condensate may then, at adjacent heated locations, have reboiled, possibly repeatedly, and become more concentrated with respect to HCl, causing acidic corrosion and failure of the manifold stubs. TerraTherm later found that acidic corrosion of the subsurface components was widespread, with at least some corrosion evident in approximately half of the 56 heater-vacuum wells, but believes that most of the subsurface corrosion may have occurred following shutdown, rather than prior to it.

All piping components, including the wells, had been constructed of stainless steel, except for high-temperature rubber steam hose between the wells and manifolds, which exhibited no damage. TerraTherm selected materials based on past experience with the ISTD technology and the concentrations of HCl vapors that were expected, as outlined in the Design Analysis<sup>2</sup>.

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<sup>1</sup> TerraTherm, Inc. 2002. *Hex Pit Material Failure Assessment Report*. Submitted to Foster Wheeler Environmental Corporation – Program Management Contract, Rocky Mountain Arsenal, Commerce City, Colorado. April.

<sup>2</sup> TerraTherm, Inc. 2001. *Hex Pit Remediation Final (100%) Design Package*. Document No. 2001-FWENC-007. Prepared for Foster Wheeler Environmental Corporation – Program Management Contract, Rocky Mountain Arsenal, Commerce City, Colorado. March.

Substantial amounts of solid deposits of corrosion products such as metallic salts and of both amorphous and crystalline organic materials were found to have accumulated within the subsurface and aboveground piping system. It is not known to what extent such precipitates occurred during heating, versus after the thermal wells were shut off, at which point the wells cooled faster than the adjacent soil.

The acidic corrosion damage that occurred is without precedent considering all seven previous completed ISTD field projects<sup>3</sup>, five of which were performed at sites with polychlorinated biphenyls (PCBs) being present in the soil at concentrations as high as 2% by weight (20,000 mg/kg)<sup>4</sup>, and one at a chlorinated solvent site contaminated with tetrachloroethene (PCE) and trichloroethene (TCE). The Hex Pit piping design was similar to what had been proven successful at those past projects. By contrast with concentrations of contaminants present at past ISTD projects, the highest concentration of Hex reported during the various pre-remedial investigations at the Hex Pit was 1.8% (18,000 mg/kg)<sup>5,6</sup>. Nevertheless, it is recognized that at some locations, concentrations of chlorinated liquid waste within the Hex Pit were probably much higher. In several of the soil borings, tarry non-aqueous phase liquid (NAPL) pesticide wastes had been visually observed without any intervening soil (and therefore at local concentrations of approaching 100%, although no samples of such materials were analyzed). TerraTherm now believes that heating enabled the pesticide NAPL to hydrolyze to HCl as it flowed into the heater-vacuum wells, or after it flowed into them, but in either case before it could undergo a significant amount of in-situ treatment within the soil as had been expected based on past ISTD projects. Hot aqueous HCl then corroded the piping, as confirmed by subsequent metallurgical testing.

After reconsidering what happened, it is noteworthy that as confirmed through interviews of site workers, thin-walled drums of liquid pesticide wastes had been dumped directly into the Hex Pit when it was filled in the early 1950s, whereupon most broke and some limited infiltration into the soil occurred. The liquid waste was then allowed to cool and harden, after which it was covered with lime and soil. The resulting occurrence of neat layers or lenses of highly chlorinated tar in between layers of soil is an unusual condition whereby the tar bodies did not occupy a porous medium. As such, the heated tar was apparently able to flow unimpeded into heater-vacuum wells. This effect was not anticipated.

Another contributing factor was the horizontal drilling performed by another subcontractor to FWENC, after construction of the ISTD well field but prior to the start of ISTD heating. During the drilling of three horizontal wells beneath the Hex Pit in February 2002, TerraTherm observed a number of “frac-out” incidents. The horizontal

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<sup>3</sup> Stegemeier, G.L., and Vinegar, H.J. 2001. “Thermal Conduction Heating for In-Situ Thermal Desorption of Soils.” Ch. 4.6-1 in: Chang H. Oh (ed.), *Hazardous and Radioactive Waste Treatment Technologies Handbook*, CRC Press, Boca Raton, FL.

<sup>4</sup> France-Isetts, P. 1998. “In Situ Thermal Blankets and Wells for PCB Removal in Tight Clay Soils,” *Tech Trends*, EPA Region 7. (February, 1998). Available at: <http://clu-in.org/products/newsltrs/TTREND/tt0298.htm>

<sup>5</sup> ENSR Corporation. 1999. Hex Pit Site Characterization Report, Rocky Mountain Arsenal, Commerce City, Colorado. Doc. No. 2840-005-500. August.

<sup>6</sup> Tetra Tech EMI. 2001. Draft Screening Investigation Report, Rocky Mountain Arsenal, Commerce City, Colorado. January.

drilling method involved injection of drilling fluids (e.g., water and drilling mud) into each borehole under high pressure for the purpose of advancing the borehole and clearing the cuttings from it. Resistance at the cutting head can cause the drilling fluids to over-pressurize. A frac-out occurs when the drilling fluids, rather than returning back out the entry point of the borehole, instead suddenly fracture the subsurface formation and emerge at the ground surface in a pool of fluid. TerraTherm observed such pools at several locations of the exposed soils around the ISTD well field and underneath its surface seal at several locations during the installation of the horizontal wells. The locations of the known frac-outs appear to correlate with locations of the earliest as well as the most severe cases of corrosion during ISTD operation. The first known frac-out occurred during the drilling of the westernmost horizontal well, and emerged close to the location where the first two manifold taps subsequently failed. In addition, a number of frac-outs occurred while the easternmost horizontal well was being drilled. During the Assessment, TerraTherm noticed that seven out of the nine most severely corroded heater-vacuum wells, plus the third failed manifold tap and the sole instance of a corroded heater-only well, all occurred directly above the path of that easternmost horizontal well. This seems more than can be explained by chance. TerraTherm believes that the frac-out incidents must have caused a displacement of the pit liquids, and in doing so the over-pressurization may have forced chlorinated tarry liquids into a large number of the thermal wells (the open annuli of which served as paths of least resistance providing pressure relief). Injection of tarry liquids into some of the well screens would have loaded them with corrosive materials, predisposing them to failure. Installation of these horizontal wells was not anticipated in the 100% Design and was added to the project after TerraTherm was awarded the implementation contract, without any technical input or comment from TerraTherm. The frac-outs and their effects constitute a changed condition relative to what was known about the Hex Pit prior to design and installation, one that TerraTherm could not have anticipated.

Conclusions of the Assessment Report included the following:

- (1) TerraTherm's materials and methods of construction were not defective, and were consistent with generally accepted practices in the remediation field. Furthermore, the material selections (e.g., 304 stainless steel) were reasonable based on past experience with the ISTD technology at highly chlorinated sites and with the concentrations of HCl that were expected. The subsurface component design did not, however, anticipate the potential for fluid tar and very concentrated HCl to flow into the wells screens with virtually no *in-situ* treatment or neutralization. This led to much more harshly corrosive conditions than anticipated within the aboveground piping system.
- (2) The process design was appropriate, based on what was known about the site conditions and past experience with the ISTD technology. Specifically, the aboveground piping was designed to withstand the expected concentrations of vaporous constituents emanating from the heater-vacuum wells. The system operated properly for 12 days, and the soil heated up according to expectations. Every one of the 266 wells was equipped with a heater. That, along with

extensive use of heated manifold piping and short uninsulated piping segments between the heated wells and the heated manifold piping was believed, based on past project experience, to be adequate to maintain the off-gas in the vapor state.

- (3) The combination of pre-existing subsurface conditions, changes in subsurface conditions caused by others (i.e., the “frac-outs”), and excessive heat losses within the aboveground piping due to abnormally cold weather led to unanticipated levels of acidic corrosion that TerraTherm did not and could not anticipate. Such results might have been evident had a pilot study been performed, but this step was not taken for the project. The Hex Pit project itself was somewhat experimental by nature, in that an *in-situ* remediation at such a highly concentrated chlorinated waste pit had never before been attempted. It was in large part for this reason that it was being conducted as a USEPA-SITE Program demonstration. The destruction of portions of the stainless steel piping within such a short duration of heating was unprecedented with respect to past ISTD projects conducted at similarly high temperatures and on similarly highly chlorinated compounds, and therefore unanticipated.

Had there been sufficient time and funding, TerraTherm believes that a suitable pilot test could have been designed and performed to determine what metallurgy would be necessary to prevent corrosion, and/or what modifications would need to be made to the heater-vacuum wells to address the presence of neat waste liquids. Such a pilot test, however, would have conflicted with major remedial actions scheduled for implementation in adjacent and surrounding RMA soils, and was thus FWENC and RVO indicated that it was not an option.

In May of 2002, FWENC terminated TerraTherm’s contract for the convenience of the government, i.e., without fault. Under FWENC’s direction, TerraTherm demobilized from the site, and FWENC subsequently covered the Hex Pit with an interim soil cover pending a decision on its disposition. The post-treatment sampling described in the accompanying SITE report was conducted following its placement.

## **INTRODUCTION**

The Rocky Mountain Arsenal (RMA) is located in Commerce City, Colorado, 10 miles northeast of Denver. The U.S. Army originally developed the 27-square mile facility in 1942, primarily for manufacturing chemical weapons. After World War II, parts of the facility were leased to private industry for pesticide manufacturing. RMA is one of the U.S. Department of Defense’s most complex CERCLA sites and is administered through the RMA Remediation Venture Office (RVO), consisting of U.S. Army, Shell Oil Co., and U.S. Fish & Wildlife Service.

Hexachlorocyclopentadiene (Hex) is an intermediary used in the production of pesticides and was manufactured at RMA’s South Plants Manufacturing Complex (South Plants) between 1947 and 1955 (see Figure 1). Between 1951 and 1952, distillation bottoms from the production of Hex were dumped into an unlined earthen disposal pit (the Hex Pit), located near the northern edge of the South Plants (see Figure 1). The

black, tar-like substance was placed in the pit in drums and bulk form. It has been estimated that the Hex Pit contains approximately 3,200 cubic yards (cy) of pesticide contaminated soil and waste.<sup>7</sup> Table 1 summarizes the physical/chemical properties of constituents of concern (COCs) identified in the Hex Pit.



**Figure 1 – 1999 View of RMA’s South Plants Manufacturing Complex. None of the structures shown remained at the time of the 2002 Hex Pit remediation.**

**Table 1 - Physical/Chemical Properties of Hex Pit COCs**

Hex Pit COC	Formula	MW	BP	VP
Hex	C <sub>5</sub> Cl <sub>6</sub>	272.7	239 °C	~20 mm @ 100 °C
Aldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	364.9	Similar to Hex	Similar to Hex
Isodrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	364.9	Similar to Hex	Similar to Hex
Dieldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	380.9	Decomposes before boiling	<1 mm @ 100 °C 200 mm @ 340 °C
Endrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	380.9	Decomposes before boiling	Similar to Dieldrin
Chlordane	C <sub>12</sub> H <sub>8</sub> Cl <sub>8</sub>	409.8	Decomposes before boiling	Similar to Dieldrin

MW = Molecular Weight; BP = Boiling Point; VP = Vapor Pressure.

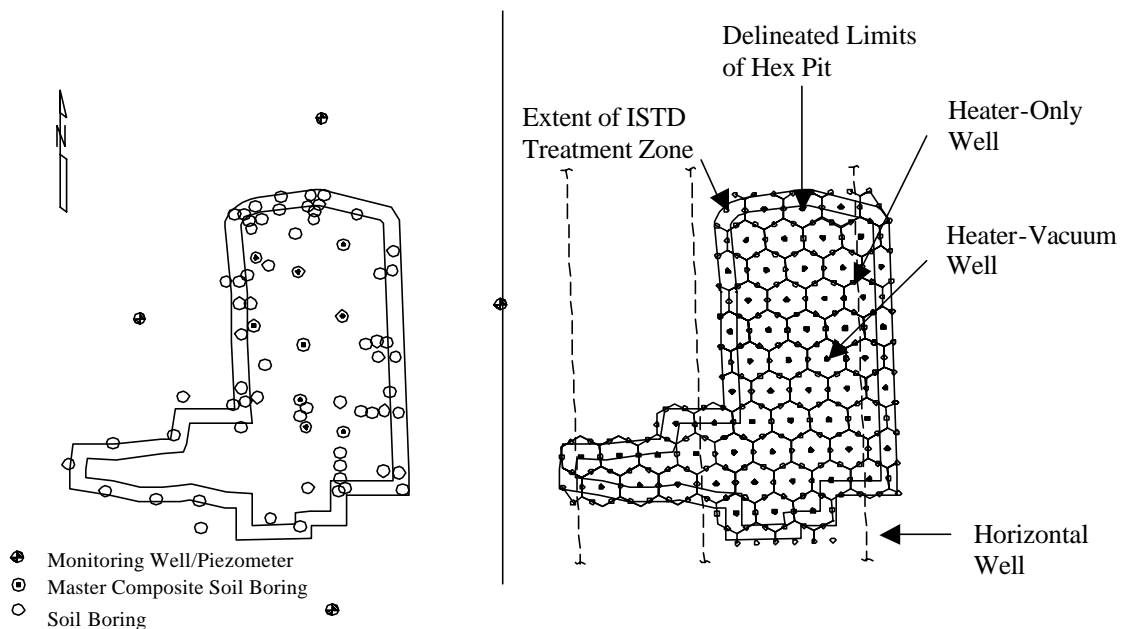
Following detailed treatability studies and design efforts, the Hex Pit Working Group, comprised of USEPA Region 8, Colorado Dept. of Public Health and Environment (CDPHE), Tri-County Public Health Dept. (TCPHD), and the RVO selected the TerraTherm *In-Situ* Thermal Destruction (ISTD) technology for remediation of the Hex Pit. As demonstrated in previous completed projects, TerraTherm’s patented ISTD technology utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil without excavation. The applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the vapor stream toward vacuum extraction wells. Because of the high inter-well temperatures possible (e.g., 300-600°C) and the fact that the vacuum extraction wells are also heater wells (at temperatures of 700-800°C), a significant percentage of the contaminant mass present in the subsurface is destroyed *in situ*. Contaminants not destroyed *in situ* are removed with the vapor stream and treated in an aboveground vapor treatment system. Based on treatability and design work, it was anticipated that >98% of the contaminant mass present would be destroyed in the heated soil at the Hex Pit, and that the remainder would be destroyed in the Air Quality Control (AQC) unit.

<sup>7</sup> TerraTherm, Inc. 2001. Ibid.

This report provides a description of pre-treatment conditions at the Hex Pit, a summary of TerraTherm’s ISTD design basis, including the remedial goals and the extent of treatment predicted, and a summary of the failure that occurred following startup, with TerraTherm’s data and evaluation of the causes of the failure.

## SITE CONDITIONS/GEOLOGY

At the time of TerraTherm’s remedial design effort in 2000-2001, a total of 117 soil borings had been performed in Hex Pit pre-design studies to identify the geology, delineate the boundaries of the pit (i.e., determine the horizontal and vertical limits of the waste), and evaluate the potential for lateral migration of the contaminants.<sup>8,9</sup> In addition, 8 piezometer/monitoring wells were installed around the pit to determine the local depth to groundwater (see Figure 2). The main portion of the Hex Pit is approximately 94 feet long (north-to-south) and 45 feet wide (east-to-west). There is also a narrow 10 foot wide portion that runs approximately 55 feet to the west of the southern portion of the pit. For design purposes, the vertical extent of the pit and the depth to groundwater were approximately 10 and 14 feet, respectively.



**Figure 2 – Hex Pit Delineation and ISTD Heater/Heater-Vacuum Well Layout. a) Locations of soil borings used to delineate limits of Hex Pit and to produce Master Composite for Treatability Study; b) Positions of thermal wells within and outside delineated limits of Hex Pit, and of horizontal wells installed beneath ISTD well field.**

The Hex Pit was excavated in alluvial material generally consisting of silty to clayey sand. The alluvial material extends to a depth of approximately 25 feet.

<sup>8</sup> ENSR Corporation. 1999. Ibid.

<sup>9</sup> Tetra Tech EMI. 2001. Ibid.

Underlying the alluvial material is the Denver Formation bedrock, which consists of weathered clayey sandstone and sandy shale. Material within the pit consists of cover material (a mixture of sand, gravel, and silt) and native soil and/or imported fill mixed with waste material.

FWENC contracted with ENSR in 1999 to perform a pre-design site characterization and treatability study. The authors of this report were employed by ENSR at the time. The lead author assembled and analyzed a Master Composite sample for the purpose of developing an average concentration of chlorinated pesticides (i.e., the COCs) within the Hex Pit. In the presence of SITE Program staff, the lead author constructed the Master Composite by mixing the entire soil column (a mixture of soil and waste material) collected from nine soil borings installed along three transects through the Hex Pit (three borings per transect). Table 2 presents the average pretreatment concentrations of COCs in the Master Composite. Although pretreatment concentrations of Polychlorinated Dibenzo-Dioxin/Furan (PCDD/F) congeners in the Hex Pit were non-calculable due to matrix interferences, the average PCDD/F concentration in soil expressed in units of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) Toxicity Equivalence (TEQ) was estimated to be at least 120 ng/g. Prior to this finding, the presence of PCDD/Fs in Hex Pit wastes had not been known, nor were PCDD/Fs stipulated as COCs during the ISTD design or implementation.

## REMEDIAL GOALS

The target performance goal set by the RMA RVO and the Hex Pit Working Group for application of TerraTherm’s ISTD technology at the Hex Pit was to achieve a 90% destruction and removal efficiency (DRE) for each of the COCs (see Table 2). The 90% DRE goals were calculated based on the average COC concentration in the Master Composite sample (see Table 2). An additional objective critical to determining the success of ISTD at the Hex Pit was evaluation of whether the technology could achieve the RMA human health evaluation (HHE) cleanup criteria for COCs in soil within the treatment area (see Table 2).

**Table 2 – COC Concentrations in Master Composite and ISTD Performance Goals**

Hex Pit COC	Master Composite Average Concentrations <sup>1</sup> (mg/kg)	Human Health Exceedance Criteria (mg/kg)	Target Performance Goal 90% DRE (mg/kg)
Hex	7,600	1100	760
Aldrin	<170	71	N/A
Chlordane (total)	670	55	67
Dieldrin	3,100	41	335
Endrin	<280	230	N/A
Isodrin	<200	52	N/A

<sup>1</sup> Average of duplicate samples from Master Composite Pre-Treatment. Less-than sign indicates concentrations were less than the stated detection limits.

## TREATABILITY STUDY

A bench-scale treatability study designed by ENSR and performed by an independent laboratory (Kiber, a division of Kemron) was intended to simulate the ISTD process and enable analysis of key process parameters including temperature and off-gas concentrations. Hex Pit composite samples were heated in an 8-in. wide x 2-in. high x 14-in. long test cell to temperatures of 300-500°C over a 30-hr period. DREs exceeded

99.5% for the COCs (Table 3), with the mass balance indicating that >99% of the DRE was attributable to in-situ destruction.<sup>10</sup>

**Table 3 – Treatability Study: Comparison of Pre- and Post-Treatment Results**

Hex Pit COC	MC Pre-Treatment Avg. Concentrations (mg/kg)	HHE Criteria (mg/kg)	TPG Criteria (mg/kg)	Treated @400 °C (mg/kg)	Treated @300 °C (mg/kg)	DRE %
Hex	7,600	1,100	760	2.80	2.80	99.981
Aldrin	<170	71	N/A	3.39	3.39	NC
Isodrin	<200	52	N/A	3.96	3.96	NC
Dieldrin	3,100	41	335	2.50	2.50	99.960
Endrin	<280	230	N/A	5.63	5.63	NC
Chlordane (total)	670	55	67	2.50	2.50	99.610

MC – Master Composite

HHE – Human Health Evaluation

TPG – Target Performance Goal

DRE – Destruction and Removal Efficiency

NC – Not calculable

N/A – Not applicable

Additional findings of the treatability study included the following:

- Permeability of the soil/waste in both the composite samples became much greater (e.g., 10,000 to 100,000-fold increase) following treatment. This was primarily due to a desiccation of the clay and removal of organic material, and is an important benefit in low permeability soils as the increased permeability allows efficient and effective vapor capture and treatment.
- Analyses of post-treatment samples indicated that ISTD also has the potential to destroy >90% of the PCDD/F isomers tentatively identified at the Hex Pit site.
- Steam distillation and volatilization were not significant removal mechanisms of the site COCs and detected PCDD/Fs. Instead, most of these compounds were destroyed within the soil (i.e., *in situ* within the test cell).
- ISTD combined with vapor treatment processes (flameless thermal oxidation; carbon adsorption) having an accumulative efficiency of >99.99999 % can be expected to produce a 2,3,7,8-TCDD TEQ emission rate of less than 0.002 ng/m<sup>3</sup>. This emission rate is five orders of magnitude less than published discharge rates from municipal solid waste incinerators and two orders of magnitude less than the recently promulgated Maximum Achievable Control Technology (MACT) standards for new hazardous waste incinerators.

These results are consistent with past ISTD field and laboratory results.

### ISTD DESIGN FOR HEX PIT

Under contract to and oversight of FWENC, TerraTherm prepared the remedial design of the Hex Pit ISTD system, beginning in 2000. The ISTD design for the Hex Pit was developed based on the results of the treatability studies and consideration of the following design criteria: 1) Target treatment temperatures, 2) Heating duration, 3) Spacing between wells, 4) Power input, and 5) Above ground treatment.

<sup>10</sup> ENSR. 2000. *Hex Pit Treatability Study Report*, Rocky Mountain Arsenal, Commerce City, CO. February.

TerraTherm selected the target treatment temperature (325°C) based on consideration of the boiling points of the COCs (Table 1) and how the vapor pressures and reaction kinetics (e.g., pyrolysis and oxidation reaction rates) vary as a function of temperature. The spacing between wells and the heating duration were designed to optimize the cost of well installation and the cost of heating (a function of power consumption and treatment and operational costs). Consideration was also given to the capacity of the soil to accept heat when dry, as the upper limit of the amount of power or heat that can be input at a well is a function of the soil's dry thermal conductivity and diffusivity. TerraTherm also conducted a field trial of the thermal wells at a clean site as a component of the Hex Pit remedial design program.

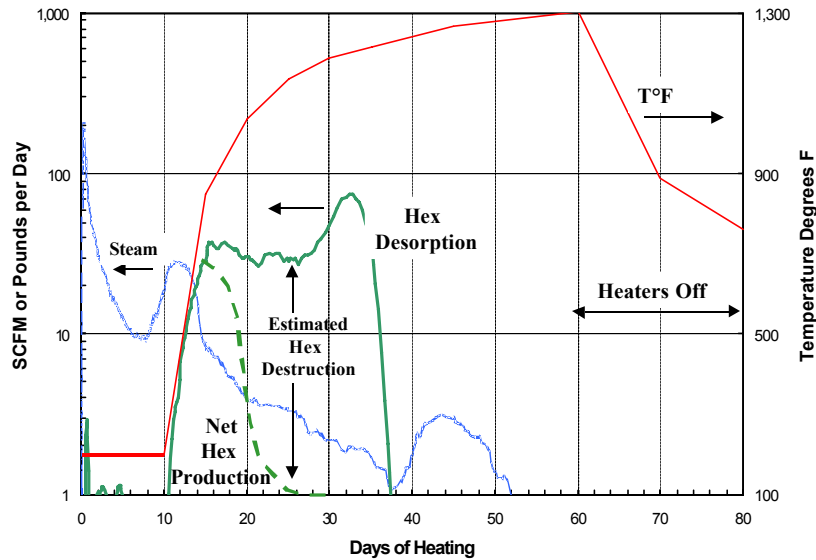
## Numerical Modeling

TerraTherm commissioned a three-dimensional, multiphase, multicomponent, non-isothermal numerical model to simulate the behavior of water and the COCs in the subsurface as a function of temperature and to aid in the design of the Hex Pit ISTD system.<sup>11</sup> The model also provided valuable predictions of COC loading during various phases of the ISTD treatment process at the Hex Pit. These phases included: 1) Heat up of the treatment area (increase in temperatures from ~20°C up to 100°C), 2) Boiling off of the soil moisture within the treatment zone (initial steam production or steam drive, temperatures at 100°C), 3) Superheat phase (temperatures from 100°C to >325°C), and 4) Cool down.

Figure 3 presents an example of the model's prediction of soil temperature immediately adjacent to a heater-vacuum (H-V) well and the steam and hex production from one of the H-V wells during ISTD treatment at the Hex Pit. Figure 3 indicates that the initial heating was predicted to be rapid and that steam production (corresponding to temperatures of approximately 100°C) was expected to be significant during the first 10 days. The initial steam flood represents the boiling off of the soil moisture present within the Hex Pit at locations adjacent to the H-V wells. Following removal of this water, temperatures increase above 100°C. Some steam continues to be produced after the initial steam flood, and represents water entering the H-V well from points farther from the well, and eventually includes water entering the treatment zone from the underlying aquifer. A small amount of hex was expected to be produced at the tail end of the initial steam flood as a result of steam stripping. At the predicted end of the primary steam flood (~day 11), temperatures at the H-V wells were expected to rapidly increase up to peak operating temperatures (600-700°C) and continue through the ensuing superheat phase of the ISTD process. After day 18 (corresponding to H-V temperatures of approximately 1000°F or 540°C), most of the hex was expected to be destroyed *in situ* and no longer produced in significant amounts. Dieldrin and the other similar COCs are known to decompose at these temperatures and were expected to be destroyed *in situ*. The superheating of the subsurface is responsible for the very high *in situ* destruction removal efficiencies predicted for the Hex Pit ISTD system. These simulation results agreed with the bench-scale treatability studies described earlier.

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<sup>11</sup> Kuhlman, M. 2000. *Simulations of In Situ Thermal Desorption at Rocky Mountain Arsenal Hex Pit*, Prepared for TerraTherm, Inc., by MK Tech Solutions, Inc., Houston, TX.



**Figure 3 – Simulated Performance of the Hex Pit ISTD System**

The figure can be interpreted in the following manner: Water is predicted to boil at the heater-vacuum well for ten days, during which the soil temperature immediately adjacent to the heater-vacuum well (red curve) is 199°F (water boiling temperature at 20 inches vacuum at Denver’s average atmospheric pressure). Around day 10, when enough pore water has been produced as steam (blue curve), the temperature begins to rise, the near-heater soil volume dries out, and hex production (dashed green curve) begins. The production rapidly rises as Hex is vaporized in the steam. Hex’s partial pressure in the steam at day 12 is about 0.01 ppm. About day 14, as the temperature of the soil adjacent to the heater-vacuum well reaches 700°F, steam pyrolysis of Hex becomes important. Thus, while Hex desorption (solid green curve) continues to increase for over 20 days, the concentration of Hex in the produced gases decreases with the increasing temperature of the soil adjacent to the heater-vacuum well. Only traces of Hex are being produced by the time the soil adjacent to the heater-vacuum well reaches 1,000°F (20 days). The temperature of the soil adjacent to the heater-vacuum well continues to rise to 1300°F before the heaters are turned off. Approximately 99% of the Hex that is desorbed is predicted to be destroyed *in-situ* or in the heater-vacuum well. Courtesy of MK Tech Solutions, Houston, TX.

TerraTherm selected a design heating duration of 60 to 70 days at a thermal well spacing of 6.0 ft, with a power input rate of 315 W/ft in the non-boosted segment of the heaters (0.5 to 10.0 ft bgs), and 400 W/ft in the boosted segment (10.0 to 12.0 ft bgs). To reduce and spread out the anticipated peak production of steam, TerraTherm planned to start up the well field in two to three phases several days apart. Thus, the overall period TerraTherm allotted for heating was 85 days.

### **Predicted Vapor Production and Acid Gas Neutralization**

TerraTherm designed the Hex Pit AQC unit by considering the amount of vapor produced, the peak COC loads, the total amount of COC expected, the degree of treatment required (air discharge permit requirements), the need for acid gas treatment, and the criteria that dioxins not be produced. As a rule of thumb, each kilowatt of power delivered to the subsurface is capable of generating 1 cubic foot/minute (CFM) of steam. The Hex Pit AQC unit also included an acid-gas scrubber because of the levels of HCl (e.g., 100s of ppm) that TerraTherm expected to be produced by the ISTD system. The production of HCl, and the need for acid-gas treatment was determined based on the nature of the hydrocarbons being treated (i.e., ISTD of chlorinated compounds was expected to produce HCl), their concentrations, and the degree of natural acid-buffering

capacity of the soil (i.e., calcium [Ca<sup>+2</sup>] and iron [Fe<sup>+3</sup>] present in the soil). TerraTherm calculated the soil's buffering capacity based on concentrations in the Master Composite soil of 98,500 mg/kg for Ca<sup>+2</sup> and 28,500 mg/kg for Fe<sup>+3</sup>. Even after assuming that only 20% of the buffering capacity would be accessible to HCl vapors, it was estimated to be capable of providing several times the required neutralizing capacity, when compared to the total amount of chloride present within the Hex Pit.<sup>12</sup> It was thus expected, based on past experience, that the presence of these buffering agents would result in neutralization *in-situ* of a very high percentage of the HCl vapors generated *in-situ*.

## Materials of Construction

TerraTherm's design utilized materials and associated methods of construction consistent with generally accepted practices in the remediation field. Furthermore, the material selections (e.g., 304 stainless steel well and manifold piping) were based on past experience with the ISTD technology as successfully used at previous ISTD field projects, five of which were performed at sites with polychlorinated biphenyls (PCBs) being present in the soil at concentrations as high as 2% by weight (20,000 mg/kg).<sup>13</sup> In contrast with concentrations of contaminants present at past ISTD projects, the highest concentration of hex reported during the various pre-remedial design investigations was 1.8% (18,000 mg/kg).<sup>14,15</sup> Material selections were also based on the concentrations of hydrochloric acid vapors that were expected (e.g., 100s of ppm), as mentioned in the previous paragraph. The adverse effects of installing horizontal wells beneath a completed ISTD well field and the resulting frac-out events were not taken into consideration, since these horizontal wells were not even contemplated during the Hex Pit ISTD remediation design period. The subsurface component design did not incorporate the possibility that neat tar and/or very concentrated liquid HCl would flow into the wells screens with virtually no *in-situ* treatment or neutralization. The actual subsurface corrosion conditions encountered were thus much harsher than had been anticipated.

## Overall Design and Installation

TerraTherm's final design of the Hex Pit ISTD system<sup>16</sup> consisted of 266 thermal wells, including 210 heater-only and 56 heater-vacuum wells installed in a hexagonal pattern at 6.0 foot spacing and to a depth of 12.5 feet bgs (see Figures 2 and 6). The treatment zone was to be heated over an 85-day period to inter-well temperatures of at least 325°C, under an applied vacuum of 20 inches of water. A surface seal consisting of 6 inches of mineral wool insulation board sandwiched between a vapor barrier and a rain

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<sup>12</sup> TerraTherm, Inc. 2001. Ibid.

<sup>13</sup> France-Isetts, P. 1998. "In Situ Thermal Blankets and Wells for PCB Removal in Tight Clay Soils," *Tech Trends*, EPA Region 7. (February, 1998). Available at: <http://clu-in.org/products/newsltrs/TTREND/tt0298.htm>

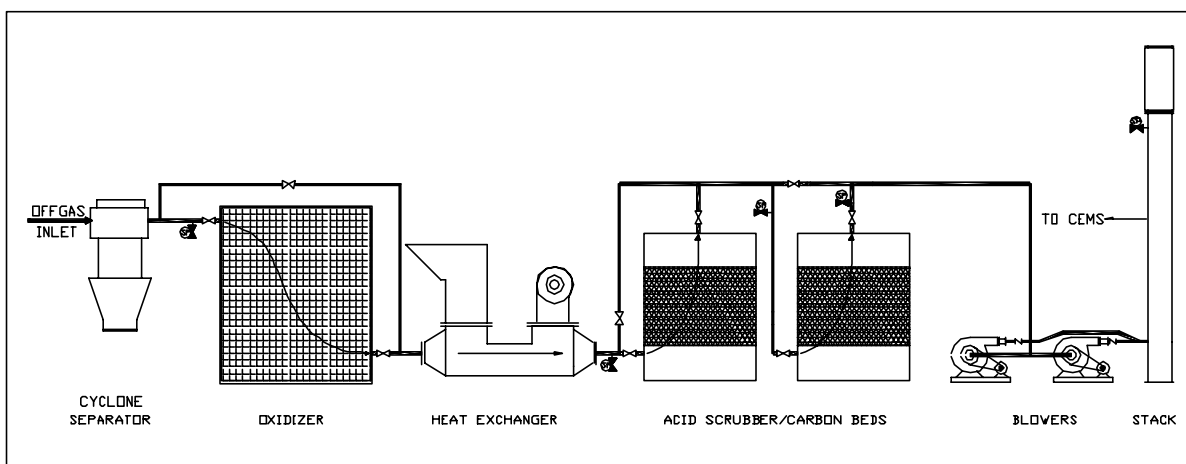
<sup>14</sup> ENSR Corporation. 1999. Hex Pit Site Characterization Report, Rocky Mountain Arsenal, Commerce City, Colorado. Doc. No. 2840-005-500. August.

<sup>15</sup> Tetra Tech EMI. 2001. Draft Screening Investigation Report, Rocky Mountain Arsenal, Commerce City, Colorado. January.

<sup>16</sup> TerraTherm, Inc. 2001. Ibid.

cover was designed to ensure that the boundaries of the treatment zone would be maintained under a net negative pressure.

The off-gas was to be treated in an AQC unit consisting of the following major components (Figure 4): cyclone separator; ThermaTrix™ Flameless Thermal Oxidizer with demonstrated capability of achieving 99.99% DRE; high-efficiency air-to-air heat exchanger; dual acid-gas scrubber beds; and dual granular activated carbon (GAC) beds. Redundant process blowers maintained the entire system under vacuum. A continuous emissions monitoring system (CEMS) at the stack was used to monitor progress of ISTD treatment and to ensure compliance with the air quality discharge limits. As a precaution, TerraTherm provided an emergency generator connected so that in the event of a loss of grid power, an automatic transfer switch would cause the generator to start within 30 seconds and continue to power the blowers and AQC equipment throughout



**Figure 4 - Process Flow Diagram of AQC System**

such an outage. This application of ISTD in conjunction with the vapor treatment processes utilizing destructive and/or adsorption technologies was expected to achieve an accumulative DRE of >99.99999 %.

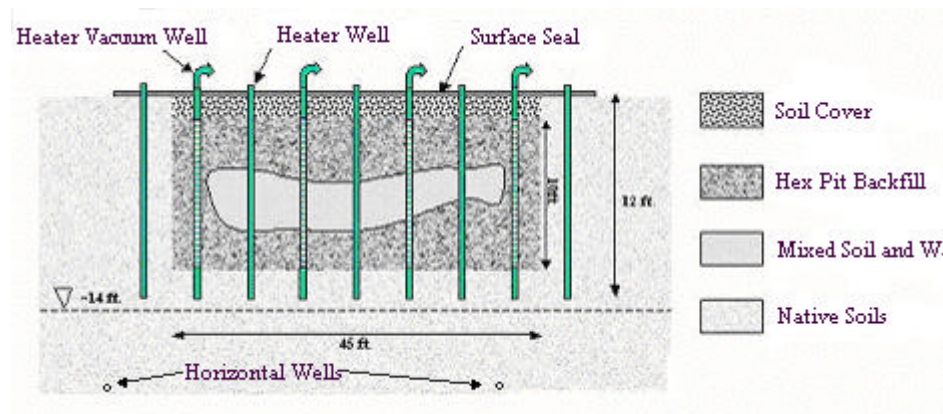
Post-treatment sampling of soil and waste material was to have been performed by FWENC and by the USEPA's SITE program. Soil samples were to be collected from within and around the perimeter of the Hex Pit, analyzed for COCs, and compared with pre-treatment samples to evaluate the performance of the ISTD treatment. Additional sampling of groundwater and off-gas vapors were also intended to be conducted as part of the USEPA's SITE program and compared with initial conditions and cleanup criteria. As discussed within the accompanying USEPA SITE Report, it was decided during the design of the SITE demonstration to focus the post-treatment soil sampling within the northern half of the Hex Pit, as soils within the southern half had been disturbed by removal of the deep foundations of former Building 571B. Pre- and post-treatment soil concentrations within the northern half of the Hex Pit were believed to be more suitable for comparison.<sup>17</sup>

<sup>17</sup> TetraTech. 2001. *Draft Quality Assurance Project Plan, In Situ Thermal Destruction Technology Evaluation at the Hex Pit, Rocky Mountain Arsenal, Commerce City, CO.*

Figure 5 presents photographs of portions of the ISTD well field and associated surface completions at the Hex Pit, while Figure 6 presents a schematic of a cross-section passing east-to-west through the ISTD treatment zone.



**Figure 5 – Photographs of Installation and Operation of Hex Pit ISTD Well Field.** Several inches of snow cover the surface seal. In the foreground of photo at left is a row of heater-only wells (shorter wells with electrical junction boxes on top). In the left foreground of photo at right is a heater-vacuum well (taller well with black vapor extraction line leading into jacketed and insulated horizontal manifold piping). The AQC system in the background of the photo at right includes thermal oxidizer in rear center (behind light stand); blowers and stack are at right.



**Figure 6 – Typical Cross-Section through the Hex Pit ISTD Treatment Zone,** looking from south towards north. During installation of the horizontal wells by others, a number of “frac-outs” occurred, several above the eastern-most horizontal well. Subsequently, during the Failure Assessment, seven out of the nine most seriously corroded heater-vacuum wells were found to be in column “P”, located almost directly above the eastern-most of the horizontal wells. It is believed that the “frac-outs” forced movement of hex fluids into the heater-vacuum well annuli prior to heating, compromising their operation.

## **ISTD IMPLEMENTATION, CESSATION AND DAMAGE ASSESSMENT Chronology Leading to Curtailment of Operation**

TerraTherm's installation of the heater and heater-vacuum wells, above ground electrical and piping systems, the surface seal, and the off-gas treatment system components began in November 2001 and was completed by February 15, 2002. System shakedown followed over the next two weeks. Startup of the ISTD treatment system began on March 3, 2002. Treatment had been expected to occur for 85 days and to be completed by the end of May 2002, but was curtailed after only 12 days of heating. The events leading up to this cessation, and the reasons for it, are described below.

### **Frac-Out Events**

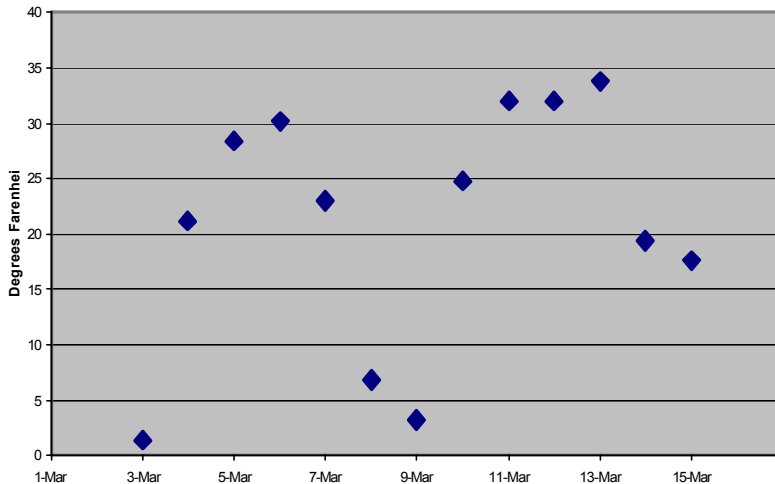
Prior to the start of ISTD heating operation, in February 2002, a drilling subcontractor to FWENC installed three horizontal wells beneath the completed ISTD well field (refer to locations indicated in Figure 2b and Figure 5), during which "frac-out" events occurred that resulted in emergence of drilling fluids around the ISTD well field and beneath the ISTD surface seal at a number of known locations. The horizontal wells were an afterthought on the part of FWENC, intended to enable the water table to be depressed in the event that wet weather caused the groundwater table to rise to near the bottom of the Hex pit during ISTD. TerraTherm agreed with this in concept, but did not participate in the design or implementation of the drilling itself, nor was TerraTherm consulted on the drilling methods and their possible impacts on the ISTD project. The horizontal drilling method that FWENC selected involved injection of drilling fluids (e.g., water and drilling mud) into each borehole under high pressure for the purpose of advancing the borehole and clearing the cuttings from it. Resistance at the cutting head can cause the drilling fluids to over-pressurize. A frac-out occurs when the drilling fluids, rather than returning back out the entry point of the borehole, instead suddenly fracture the subsurface formation above it and emerge at the ground surface in a pool of fluid. TerraTherm observed such pools around the completed ISTD well field and at several locations underneath its surface seal during the installation of the horizontal wells. TerraTherm reported these events to FWENC on February 19, 2002 in a Notice of Changed Conditions. FWENC's response was to downplay the significance of the frac-outs.

The locations of the known frac-outs appear to correlate with locations of the earliest as well as the most severe cases of corrosion during ISTD operation. The first known frac-out occurred during the drilling of the westernmost horizontal well, and emerged close to the location where the first two manifold taps subsequently failed. In addition, a number of frac-outs occurred while the easternmost horizontal well was being drilled. In the Assessment Report, TerraTherm reported that seven out of the nine most severely corroded heater-vacuum wells, plus the third failed manifold tap and the sole instance of a corroded heater-only well, all occurred directly above the path of that easternmost horizontal well. Considering the relatively large number of heater-vacuum wells (56) and heater-only wells (210), this linear co-location of frac-out events and wells showing severe corrosion is, in TerraTherm's opinion, more than can be explained by chance.

TerraTherm believes that the over-pressurization that produced the frac-out incidents must have caused a displacement of the pit liquids, and in doing so the injection pressure may have forced tarry liquids into a large number of the thermal wells (the open annuli of which would have served as paths of least resistance providing pressure relief). Injection of tarry liquids into some of the well screens would have pre-loaded them with hex and other chlorinated pesticides. Upon being heated, they quickly hydrolyzed within the well annuli into boiling HCl. We believe that this, in large part, led to the premature destruction of the piping system. Absent the frac-out events, hydrolysis of the pit contents would have occurred outside the heater-vacuum wells, and the HCl that would have arrived there would have been in the vapor phase, which is what the materials of construction were designed to withstand. 304SS is far more resistant to HCl in the vapor phase than as a liquid. There would also have been more in-situ neutralization of acid gas by buffering within the soil than could occur with acidic liquids forming directly in the wells. The frac-outs and their effects constitute a changed condition relative to what was known about the Hex Pit prior to design and installation.

### Weather Conditions

Ambient temperatures during the last week of shakedown/pre-heating and during ISTD operation were abnormally cold. Minimum ambient temperatures for the period March 3 through March 15, 2002 are presented in Figure 7. These cold ambient temperatures, along with average winds of 10-15 mph, had the effect of reducing the near-surface soil temperatures prior to the start of heating. However, more significantly, these cold temperatures may have resulted in greater than anticipated heat losses in the vapor tees, the short (approx. 2”) exposed stubs of the manifold taps, and flexible hoses connecting these points, based on the field observations described in subsequent sections. This, we believe, contributed to the condensation of steam, pesticide vapors and HCl vapors and resulting accumulation of acidic, corrosive liquids at such locations.



**Figure 7 – Minimum daily temperatures during the period of ISTD operation as reported by the National Weather Bureau, Denver, CO. Startup began on March 3, and ISTD operation continued until March 15, 2002.**

## **ISTD Startup and Discovery of Initial Corrosion**

Prior to energizing the well field, TerraTherm pre-heated the oxidizer and energized all of the manifold insertion heaters to pre-heat the well field piping manifold. The off-gas treatment system was drawing only ambient air during this pre-heating period. On March 3, 2002, after all 56 of the heater-vacuum wells were energized and reached their operating temperature, the fresh air inlet valves on the manifold lines were gradually closed to allow vapors to be drawn from the subsurface into the AQC system. On March 5, TerraTherm also energized 84 heater-only wells in the southern third of the well field (rows 17-24). Thermocouple data (reviewed below) indicated that the well field was heating up as expected, and the AQC system was also functioning well.

On March 15, 12 days into the initial heating period, TerraTherm operators reported that two 1-½” diameter manifold pipe taps (i.e., vertical “tees”) on manifold leg #9 (southwestern quadrant of the well field) had tipped. These 304SS taps were located where the steam hose leading from two adjacent heater-vacuum wells connected down into a horizontal piping manifold. Each of the piping manifolds was being heated to >200°C (>390°F) with insertion heaters running the lengths of the manifolds, which were in turn insulated with calcium silicate insulation and jacketed with stainless steel. The lower ends of the manifold pipe taps, situated inside the manifold insulation, had been eaten away by corrosion.

## **ISTD Shutdown and Actions Taken**

TerraTherm recognized this corrosion as a potentially serious problem that, if allowed to continue, might jeopardize the ability to collect and treat gases that were being generated from the heated subsurface. Therefore, TerraTherm shut down power to the thermal wells, but continued to operate the AQC system for the next two days. Air sampling and analysis confirmed that none of the stipulated hourly rolling average air quality standards for off-gas emissions had been or were ever exceeded. Site workers were protected from exposure to contaminants through appropriate use of Personal Protective Equipment throughout the damage assessment that followed.

With the concurrence of FWENC, the RVO and the various Regulatory Agencies, TerraTherm commenced a comprehensive assessment of the damage to its piping system, the results of which TerraTherm presented in a document entitled “Hex Pit Material Failure Assessment Report” [Assessment Report]<sup>18</sup>.

## **Evaluation of the Initial Corrosion**

TerraTherm found a total of three manifold taps in the aboveground piping that failed due to acidic corrosion during operation. It appeared that those failures were due to a combination of a much higher-than-anticipated production of hydrochloric acid (HCl) coming out of the heater-vacuum wells, and, in the abnormally cold, near-zero weather, higher-than-anticipated heat losses from the uninsulated piping connections

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<sup>18</sup> TerraTherm, Inc. 2002. Ibid.

located between the hot thermal wells and the heated manifolds. More specifically, the upper ends of the vertical well field heaters within each heater-vacuum well terminated at least 12 inches beneath the surface seal, while the connection from the wellhead to the heated horizontal manifold consisting of heat-resistant flexible rubber steam hose (visible in Figure 5) ranged from approximately 4 to 8 ft in length. This arrangement, coupled with the low ambient temperatures, enabled the temperature of the vapor stream (including steam, pesticides and HCl) at such portions of the piping to drop below the condensation points of the constituents.

For several days during heating, TerraTherm's operators had noted the presence of liquid condensate in a number of the flexible steam hoses, which had to be manually emptied each shift to relieve the liquid obstruction in the hoses. Accumulation of some liquid condensate in abnormally cold weather is not unexpected during ISTD operation and has been observed on past ISTD projects. Nevertheless, these flow restrictions, along with the much higher-than-expected production of HCl (at percent levels) from the heater-vacuum wells, are believed to have led to the corrosion of the failed manifold taps.

Under normal operating conditions, the vapor stream velocity through the manifold taps was designed to be fairly high, estimated to be on the order of 24 ft/sec. This flow velocity, along with the imposed vacuum of 20 to 30" water column should have been enough to sweep liquid droplets and corrosive vapors rapidly through the taps and minimize formation of a liquid condensate film on the interior walls of the manifold tap. It appears, however, that as the flow obstruction became more substantial, the vapor flow through the affected taps was reduced and eventually may have ceased. Without the sweeping effect of the high velocity vapor stream, corrosive liquids may have been able to condense in the approximately 2" length of exposed, uninsulated manifold tap that protruded above the manifold pipe insulation, where the temperature dropped below the condensation points of steam and/or contaminants. Boiling aqueous HCl is approximately 1000 times more corrosive than HCl in the vapor phase. A very aggressively corrosive liquid film may have condensed on the interior wall of the uninsulated tap segment where it streamed down along the hot, insulated segment of the tap. As the liquid reached the hotter segment of the tap (or possibly entered the hot 4" manifold pipe), it is believed that the water vapor flashed to steam and carried the corrosive acid back up into the uninsulated segment of the tap where it subsequently re-condensed on the interior walls and again streamed down. Such a reflux cycle, if repeated, may have had the effect of concentrating the acid to its constant-boiling azeotrope, containing approximately 20% HCl by weight.<sup>19</sup> Metallurgical analysis of the failed taps indicated they had undergone general corrosive attack, evidenced by a reduction in wall thickness from the initial 0.125" to 0.108" over a period of several days, which is a very high rate of metal loss. Note that TerraTherm does not believe this could have occurred had the levels of HCl entering the heater-vacuum wells not been so elevated to begin with. Thus the root cause is believed to be the changed subsurface conditions, as discussed above.

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<sup>19</sup> McGraw-Hill, Inc. 1974. *Chemical and Process Technology Encyclopedia*, p. 588.

## **AQC Shutdown**

TerraTherm mobilized its Project Engineer to the site immediately upon the decision to shut down the well field heaters. Upon his arrival on March 16, 2002, he discovered the presence of approximately 200 gallons of highly acidic (pH 0) condensate in the knockout pot located between the heat exchanger and the dry scrubber vessels, and proceeded to transfer it to the condensate storage tank that was on-site for this purpose. While pumping an additional 300 to 500 gallons of rinse water through the knockout pot and into condensate storage tank, some liquid was accidentally drafted over into Scrubber Bed #1 and accumulated at the bottom of the bed. The Project Engineer immediately bypassed Scrubber Bed #1 due to the excessive pressure drop created by the liquid accumulation.

On March 17, attempts were made to drain water out of Scrubber Bed #1, and later to dry it out using hot air from the oxidizer, which resulted in excess heat inadvertently arriving at Carbon Bed #1. A brief carbon monoxide excursion was noted, and the elevated carbon bed temperature tripped the system interlock. The TerraTherm Operator immediately isolated the carbon and scrubber beds, closed the well field manifold valves, and shut down the blower. Upon investigation, TerraTherm concluded that incomplete combustion (a carbon vessel fire quenched by lack of air) had briefly occurred in Carbon Bed #1. Neither the ISTD well field nor the AQC system were subsequently restarted during the Assessment phase that followed.

## **Well Field Temperatures**

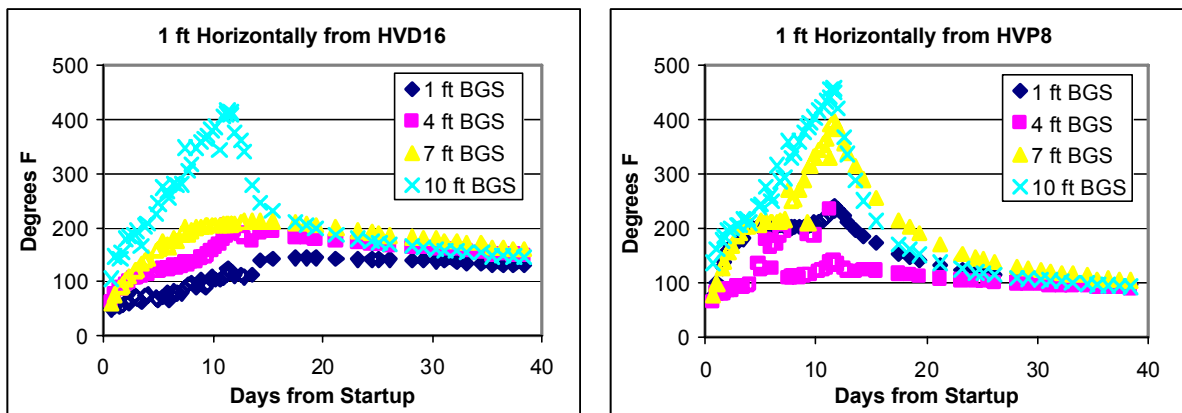
It is pertinent to review the data collected by the well field thermocouples throughout the period leading up to and following cessation of the ISTD system. Following is a summary of the well field temperature data trends:

One heater-vacuum well in the north end of the field (HVD4) had been outfitted with thermocouples within the heater can, in the annulus between the heater can and the well screen, and within the sand pack just outside the well screen. A heater-only well at the southern end of the pit (HOO16), located just south of the zone where heater-only wells were operating, was also outfitted with thermocouples just outside the well screen. Within 24 hours in the instrumented heater-vacuum well at the northern end of the site (HVD4), the temperature inside the heater can was over 900°F, while the temperature of the annulus between the vacuum well screen and heater can was nearly 700°F, and the temperature in the sand pack just outside the well screen was over 100°F. However, the soil temperature just outside the instrumented heater-only well just north of the southern end of the pit (HOO16) remained between 50 and 60°F for approximately 5 days.

Heating in the southern third of the pit (Heater Rows 17-24) where heater-only and heater-vacuum wells were all operating was progressing normally, and appeared to be slightly ahead of schedule relative to what had been simulated during the Remedial Design. By Day 5 of heating, soil temperatures measured in the south end thermocouple arrays located approximately 2 feet from the wells and 7-10' deep were at or above

150°F, while the shallower (1 to 4' deep) thermocouples were approximately 100-120°F. At this time, soil temperatures approximately 3 feet from the wells were 75-100°F. By heating Day 10, temperatures measured in thermocouples located 2 feet from south-end wells were at or above the boiling point of water at the 5280-ft elevation of RMA (200°F), and temperatures 3 feet from the wells were very nearly 200°F, again with the exception of the 1'-deep zone which was lagging 20 to 30 degrees behind.

In the northern two-thirds of the pit (Heater Rows 1-16) where only heater-vacuum wells were operating, the temperature distributions were somewhat more irregular, as this area did not have the benefit of superposition of heating, as did the fully operational southern end. By Heating Day 5, thermocouples located at the southern edge of that portion of the pit, approximately 1 foot from heater vacuum well HVD16 (Figure 8a) were approximately 250°F at 10' depth, and ranged from 120 to 170°F at the 4 to 7 foot depth ranges, while the near-surface temperature was approximately 70°F. By the end of the 12-day heating period, the 10'-deep thermocouple at this location had reached a temperature of 416°F, and the mid-depth thermocouples were just over 200°F, while the shallow thermocouple was lagging behind at approximately 120°F. Further north in the field, temperatures within 1 foot of an energized heater-vacuum well in Row 8 (HVP8) on Heating Day 5 were at or above 200°F (Figure 8b), with the exception of the mid-depth 4' deep thermocouple reading, which was approximately 125°F. This may be indicative of locally saturated conditions in the mid-depth region. In contrast, soil temperatures measured by thermocouples installed in the far northern end of the pit had typically increased only 20 to 30°F and were still below 100°F after 12 days of heating. Those locations that increased by 30°F were nearer to the operating heater vacuum wells. This rate of heating was normal and as expected.



**Figure 8a,b – Representative temperature data from thermocouple arrays located 1.0 ft horizontally from each of two heater-vacuum wells. Maximum temperatures were achieved on day 12, at which time heaters were turned off. Deeper locations were generally hotter, attributable to the boosted wattage in the lower two feet of the heaters. After shutdown, temperatures equilibrated and gradually declined.**

Following shutdown of the well field heaters, the soil in the pit remained hot. Thermocouple temperatures in the southern portion of the pit generally held steady or

dropped only a few degrees for the first several days after the heaters were shut down. In some cases, the temperatures actually increased as a result of equilibration from the radially advancing heat front to adjacent, cooler soil. One week after shutdown of the heaters, soil temperatures in the southern end of the well field were still within 2 to 10 degrees of where they had been prior to shutdown, ranging from 170 to 210°F, with a few exceptions. In the northern end of the pit where only the more widely-spaced heater-vacuum wells were operating, temperatures changed more dramatically. Although some soil temperatures increased slightly as a result of equilibration, the temperature of the soil in the vicinity of the operating heater-vacuum wells generally dropped 50 to 100°F or more within 1 week of shutdown. As expected, thermocouples that were more distant from an operating heater-vacuum well, where the soil temperature was only 20 to 40°F above ambient soil temperatures did not exhibit as significant a drop in temperature.

### **Post-Shutdown Findings**

As reported in the Assessment Report, TerraTherm made numerous observations concerning the post-shutdown conditions within the ISTD well field. These included most prominently blockages within the aboveground vapor tees, and blockages and corrosion within subsurface portions of the heater-vacuum wells. The following paragraphs summarize these findings.

Approximately 30 of the 56 vapor tees (located near the tops of each of the heater-vacuum wells) were observed to have deposits and varying degrees of clogging, with 11 being completely clogged. In addition, both ends of the steam hose connecting the vapor tees to the manifold pipe taps had flanged end connections. The flanged ends of approximately 40 of the 56 flexible hoses were observed to have accumulated deposits. Of these, approximately 12 exhibited only minor accumulations of damp red or black tarry material. Eighteen of the hose end connections were more than 50% clogged, while 4 segments were found to be completely clogged. In most cases when significant clogging was observed in either the vapor tee or hose connection, it was observed in both locations.

Deposits observed ranged from yellow/orange/brown needle-like crystalline or fibrous material, to black tarry residue and red/black muddy residue, to tan/yellow/green or white powdery or cake-like material, in no particular pattern of occurrence. Based on visual observations, the yellowish fibrous material was initially believed to be dieldrin or aldrin crystals; however, laboratory testing results discussed in the Assessment Report appear to indicate that the material was comprised predominantly of Hex rather than of dieldrin or aldrin. There did not appear to be a discernable pattern of clogging in the heater-vacuum wells or flexible hoses. Significant clogging, (>50% obstruction in either the vapor tee or hose connections), was observed in heater-vacuum wells in both the fully energized southern end and the partially energized northern end of the Hex Pit.

It is not known whether these vapor tee and hose end deposits accumulated at the same time as the highly acidic liquid condensate that is believed to have resulted in failure of the manifold pipe taps described above, or whether they formed afterwards, during the period when the well field was beginning to cool. As suggested by the

thermocouple data, vapors may have continued to be produced from the still hot soils for some time after shutdown. During this time, the AQC was shut down and the well field piping manifold was isolated such that vapors could have risen into the vacuum wells and accumulated in the pipe manifold. The simulation (Figure 3) furthermore indicates that the shutdown occurred when the production of Hex was starting to peak, but prior to when Hex destruction (and therefore reduced production of Hex) would have been expected to become predominant. Thus, the presence of Hex and related deposits within the heater-vacuum vapor tees and hose end fittings, although undoubtedly exacerbated by the abnormally low temperatures, may be a transient artifact of the shutdown that would have literally evaporated and been swept into the AQC system as the well field continued to heat up, had highly acidic and corrosive liquids not compromised the piping system first. The few locations completely blocked with crystalline deposits may have experienced liquid blockage of the steam hoses first, as a precondition. Otherwise, the velocity of the vapor extraction would have tended to keep the deposits in check. It is not possible to say what fraction of the vapor tee and hose connection clogging occurred during the heating operation and what fraction occurred after the heating was shut down. Based on the loss-of-flow scenario described above, it is believed that some of the clogging occurred during the heating operation. However, the majority of the clogging is believed to have occurred after the well heaters were shut down.

TerraTherm also found that acidic corrosion of the subsurface components, including chloride stress corrosion cracking was widespread, with at least some corrosion evident in approximately half of the 56 heater-vacuum wells. Most of the subsurface corrosion probably occurred following shutdown, rather than prior to it.<sup>20</sup> This conclusion is based on the self-protective characteristics of thermal wells. As mentioned above, gaseous HCl is approximately 1000-fold less corrosive than liquid HCl. Whenever thermal wells are energized, their operational temperatures are so high (as exemplified by the very high 1000-1100°F operating temperature measured within the annulus of HVD4, and presumably representative of all the heater-vacuum wells) that liquids in contact with them will instantly flash to steam or other gases unless there is a significant source of recharge of liquid to the well. It is not believed that there was such a source of recharge within the Hex Pit. Although small, localized pockets of perched liquid were evident during the Hex Pit site investigation, most (>95%) of the volume of soil and waste was observed to be far below saturation. However, once the thermal wells were de-energized, they could no longer protect themselves. The soil and waste around them remained near the boiling temperature of water for weeks, during which it is believed that conditions remained highly corrosive. Thus the conditions following shutdown probably produced most of the subsurface damage observed during the Assessment.

### **SITE Program Findings**

TerraTherm was given the opportunity to review the final draft of the accompanying SITE Program Hex Pit Demonstration Report. It is noteworthy that the mean concentration of hex reported in Table 2-1 of the SITE report for the various

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<sup>20</sup> TerraTherm, Inc. 2002. Ibid.

“Composite Samples from SITE Pre-treatment Sampling” (8,150 mg/kg) corresponded well to the concentration of hex observed in the Master Composite (8,100 mg/kg), which was the basis for the Hex Pit treatability study and the remedial design described above.

In our comments on the final draft SITE Program Hex Pit Demonstration Report, we pointed out that given the obvious data trends, it was surprising that the authors chose not to perform a statistical evaluation of pre- versus post-treatment concentrations of dieldrin, the second most important COC, and aldrin, while instead including an evaluation of trichloroethylene, a compound that was not even included among the COCs and not present at significant concentrations. An examination of the data trends in the SITE Program data (Table 3-4, “Summary of SITE Pre- and Post-Treatment Analytical Results”) suggests that despite the short period of operation, a significant amount of *in-situ* destruction occurred with respect to dieldrin (for which the mean pre- and post-treatment concentrations were 805 and 122 mg/kg, respectively) and aldrin (mean pre- and post-treatment concentrations of 375 and 20 mg/kg, respectively).

## LESSONS LEARNED

TerraTherm learned the following lessons from this experience, and is applying them in current ISTD projects:

- Horizontal drilling should never be conducted beneath an already completed ISTD well field, especially if there is any possibility of over-pressurization leading to frac-outs.
- Include the worst-case conditions encountered in treatability studies, design calculations and simulations.
- When contemplating applications of ISTD to treat wastes that are qualitatively different than those previously encountered (e.g., a waste lagoon like the Hex Pit in which the wastes may reside as neat layers of tar, rather than as residual NAPL within a porous medium), perform a pilot test first. Such a pilot test affords the opportunity to examine the suitability of materials of construction; assumptions regarding off-gas production and loading rates; the time periods required to treat the waste at a given wattage and spacing of thermal wells; etc. Consider performing such pilot tests in worst-case locations.
- If there is a possibility that abnormally cold weather may occur during startup, insulate and/or heat as many sections of the above-ground ISTD piping as possible, without producing overheating of sensitive components.
- Lateral connections from ISTD heater-vacuum well vapor tees to the piping manifold have been re-designed to prevent sagging of the flexible connector and eliminate low-points that may serve as liquid accumulation/flow obstruction points.
- Do not assume 90% *in-situ* neutralization of acids, especially in the case of mobile, highly chlorinated NAPL.
- Use of Magnehelic gauge taps and ball valves at the vapor tee of each heater-vacuum well, while slightly more expensive, affords the ability to confirm flow from each heater-vacuum well, and to rebalance such flows under changing conditions during treatment.

## CLOSING

As mentioned in the Executive Summary, in May 2002, FWENC Terminated TerraTherm's Subcontract for the Convenience of the Government, and subsequently reached a settlement with TerraTherm that recognized no fault on the part of either party. TerraTherm is releasing this report in an effort to promote a better understanding of the conditions that led to and resulted in the cessation of this project, in hopes that future applications of the ISTD technology will benefit from what was learned.

It must be emphasized that what occurred at the Hex Pit was unprecedented relative to prior applications of the ISTD technology, five of which were performed at sites with polychlorinated biphenyls (PCBs) being present in the soil at concentrations as high as 2% by weight (20,000 mg/kg), and one at a chlorinated solvent (PCE/TCE) site. The Hex Pit ISTD piping design was similar to what had been proven successful at those past projects. By contrast with concentrations of contaminants present at past ISTD projects, the highest concentration of hex reported during the various pre-remedial investigations was 1.8% (18,000 mg/kg). Field project experience from the completed ISTD projects and laboratory treatability studies, including the treatability test performed on Hex Pit waste material, indicate that high subsurface temperatures maintained over a period of days are capable of extremely high *in situ* destruction removal efficiencies of even high boiling point contaminants such as PCBs, pesticides, PAHs and other heavy hydrocarbons. Despite high pre-treatment concentrations, post-treatment soil concentrations have typically been non-detect. ISTD thus offers a means to reliably achieve stringent cleanup goals that have not been previously possible by other *in situ* treatment technologies.<sup>21,22</sup>

## ACKNOWLEDGEMENTS

The authors wish to acknowledge Keith Bowden of TerraTherm, Inc. for supervising the ISTD construction, Glenn Anderson for supervising the Damage Assessment and demobilization, Denis M. Conley of Haley and Aldrich, Inc., Houston, TX for providing emissions-related technical support, Myron Kuhlman of MK Tech Solutions, Inc., Houston, TX for providing numerical modeling simulations of the ISTD processes, Steve Hall of Kemron Environmental Services Inc., Norcross, GA for performing the treatability study, and John LaChance of TerraTherm for support.

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<sup>21</sup> Baker, R.S., J. M. Bierschenk. 2001. "In-Situ Thermal Destruction Makes Stringent Soil and Sediment Cleanup Goals Attainable," Fourth Tri-Services Environmental Technology Symposium, San Diego, CA.

<sup>22</sup> Stegemeier and Vinegar, 2001. Ibid.