

PREMIER TECHNOLOGY APPLICATION OF VACUUM-ASSISTED THERMAL DESORPTION FOR THE TREATMENT OF RADIOACTIVE PCBs

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ABSTRACT

Materials & Energy Corporation (M&EC), a subsidiary of Perma-Fix Environmental Services, Inc., specializes in the treatment and management of radioactive RCRA and TSCA-regulated waste from DOE remediation efforts. This paper describes the demonstration process used to permit a vacuum thermal desorption unit for the treatment of PCB-contaminated, radioactive waste. A discussion of the “lessons learned” from the test, as well as a discussion of the implications for use in treatment of legacy waste, is included.

INTRODUCTION

Poly-chlorinated biphenyls (PCBs) are manufactured poly-cyclic hydrocarbons containing two benzene nuclei with a varying number of chlorines attached, depending upon the congener. PCBs are not naturally occurring and were manufactured in the U.S. by the Monsanto Corporation beginning in 1929. PCBs were highly valuable as dielectric fluids and heat sinks because of their high heat resistance and ability to withstand sustained temperature and pressure without degrading. Their use spread to various insulating materials, paint, and polymer manufacture. Over time, it was discovered their resistant nature also made them persistent, bioaccumulative environmental toxins. In 1979, the manufacture of PCBs in the United States was banned with the passage of the Toxic Substances Control Act (TSCA). With the passage of TSCA, the U.S. Environmental Protection Agency (EPA) also modified the disposal requirements for PCB waste such that most types of PCB waste required incineration prior to land disposal.

In 1997, EPA's Office of Pollution Prevention and Toxics prepared an assessment of the management of polychlorinated biphenyls (PCBs) in the U.S. The assessment was used as background for the research on persistent organic pollutants currently that was being performed by the United Nations Environment Program (UNEP). In their report to UNEP, EPA made the following statement regarding storage and disposal capacity of radioactive PCB waste:

A Canadian report states that "conversations with [U.S.] facility managers indicate that there is no shortage of commercial storage capacity in the United States". Disposal capacity also appears to be adequate, *except for radioactive PCB wastes* [emphasis

added]; as of 1994, over 50 million tons of radioactive PCB wastes were in storage awaiting disposal, and radioactive PCB wastes were being generated at a rate in excess of 5 million tons per year. In almost all other instances, permitted disposal facilities are operating below their maximum or permitted capacity. Incinerators are operating at approximately 57 to 75 percent of permitted capacity, and close to 14 million cubic yards of landfill space is or soon will be available. The remaining capacities could be used for hazardous wastes other than PCBs as well. Proposed amendments to U.S. PCB regulations regarding treatment and disposal could potentially increase the capacity while reducing disposal costs. [1]

It is apparent the EPA recognizes limited storage and disposal capacities for radioactive PCB waste has existed for quite some time. The reasons for the limited commercial capacity can generally be attributed to two factors. First, the permitting and licensing of a new radioactive waste facility is extremely complex and is subject to multiple regulatory authorities (i.e., TSCA, Nuclear Regulatory Commission (NRC)). The permitting process alone may be cost-prohibitive to a prospective new waste management facility. Second, the sensitive political implications associated with permitting these types of facilities discourage the construction of new facilities.

The U.S. Department of Energy (DOE) is the largest generator (by volume) of radioactive PCB waste in the U.S. A majority of the PCB waste generated by DOE was produced as a result of nuclear weapons production activities during the Cold War era. In a recent disposal capacity assessment (2002), DOE evaluated the volume of radioactive low-level waste (LLW), and low-level “mixed” waste (LLMW) in storage at various DOE facilities. LLMW is radioactive waste that is also subject to the Resource Conservation and Recovery Act (RCRA) and/or TSCA. The following table summarizes DOE’s reported and projected inventory of LLW/LLMW through 2070:

Table I. Summary of DOE LLW and LLMW Current and Projected Inventory through 2070 [2]

Projected Disposition	Estimated Volume by Waste Type (cubic meters)		Totals
	LLW	LLMW	
Waste Operations Disposal Facilities	1,200,000	63,000	1,200,000
Existing/Approved Environmental Restoration CERCLA Disposal Facilities	7,500,000	200,000	7,700,000
Planned Environmental Restoration CERCLA Facilities	170,000	37,000	200,000
To Be Determined	280,000	5,100	280,000
Commercial Disposal	1,000,000	150,000	1,200,000
Totals	10,100,000	450,000	10,600,000

The table does not show what percentage of the LLMW contains PCBs, but it is important to recognize that mixed waste that PCBs may be subject to multiple treatment and permitting standards, depending upon the matrix they are in and how the waste was generated. Determining the appropriate treatment standard for PCBs also requires consideration of the RCRA and NRC-regulated constituents in the waste matrix. This is a complex process.

Vacuum Thermal Desorption is a relatively new technology that uses low temperature and agitation to separate volatile and semi-volatile organic compounds from solid matrices. The volatilized organics are captured in a series of condensers and are typically undergo further treatment by a combustion or incineration unit. The solid matrix, once treated, can be declared compliant with applicable treatment standards and disposed in an appropriate land disposal facility. The process for obtaining EPA approval for the use of this technology in treating PCB-contaminated waste is functionally equivalent to that of permitting an incinerator. It involves careful planning, interaction with multiple regulatory agencies and a strong consideration of how the public will perceive the operation of such a unit in their community. Success does not come easy (or cheap), but the use of thermal desorption is likely to become one of the most preferred methods for treating LLMW because of its relatively low risk, minimal volume increase and high reliability of success.

Description of Vacuum Thermal Desorption Unit

The thermal desorber is an Advanced Process Systems® (Elrich Group) plow blender with a working capacity of approximately 550 gallons. The desorber is equipped with an integral insulated heating jacket designed to heat to a maximum internal temperature of 700°F. The heat source is a gas-fired, hot oil boiler. The range of operating pressure for the interior of the sludge dryer is from -29 inches of mercury to a maximum of +10 psig. To prevent development of explosive mixtures in the headspace of the vessel and its exhaust systems, it is equipped with a nitrogen gas injection port, capable of injecting 5 to 50 SCFM of nitrogen into the vessel headspace. Further, the main shaft seals on the system are blanketed with nitrogen. The injection port is designed and located so as to provide a nitrogen blanket inside the vessel to reduce oxygen concentration in the headspace of the reactor. (See Figure 1)



Fig. 1. Photograph of VTD unit and ancillary equipment.

The unit is equipped with a horizontal mechanical agitator with a driveshaft along the centerline of the vessel. The drive motor controls are designed to allow the unit to operate at variable speed selected by the unit operator. The radial struts extending from the central drive shaft toward the walls of the vessel have mortises, and fasteners that permit easy replacement of agitator plows (or blades), as necessary, to adapt the plow configuration and plow-to-wall clearances to different waste physical characteristics.

The thermal desorber vessel is equipped with one feed hopper mounted to a bolt flange on the top surface of the unit, a vapor dome filter housing mounted to a second flange on the top surface of the vessel and a solids discharge from the bottom surface of the vessel by way of an integrally mounted ball valve. (See Figure 2)



Fig. 2. Photograph of vertical lift and feed hopper mechanism.

Process vapors pass through a pulse back filter (pulsed with nitrogen) that utilizes high temperature ceramic cloth filter bags to prevent carry over of fine particulate solids with the vapors. The filter is jacketed with hot oil to allow the filters to maintain the same operating temperature as the vessel.

The discharge ball valve at the bottom of the desorber is connected by a bolt flange to a larger seal flange where drums or boxes are filled with treated solids. Only solids that are verified to be completely treated will be discharged. The seal flange is sized so that a drum or a box can be positioned below the discharge port and sealed. A scissor lift is used to raise the receiving container until its lip is sealed tightly against the rubber lining of the seal flange. The scissor lift and seal flange are enclosed in an air-locked enclosure.

Unit instrumentation and controls allow the monitoring of shell and interior temperatures, pressure, oxygen concentration, and electrical consumption. Specific control information is described in detail in the Monitoring Plan section of this application.

The condenser and sub-cooler assembly is capable of a cooling duty of 8.11×10^6 Btu/hr and is used to condense the volatilized organics. The assembly is supplied with cooling water from the facility's evaporative cooling tower. The condensate accumulator tank (T-26) is a sealed, vacuum rated (29" Hg), cone bottom tank constructed of 304L stainless and has a capacity of approximately 450 gallons. This vessel receives condensate from the condenser and subcooler; gases pass to the vacuum pump inlet. Any off-gas from the unit pass through a demister, carbon filter and High Efficiency Particulate Air (HEPA) filtration prior to discharge.

Waste is treated in batches. The desorber is filled with up to 550 gallons (5,000 pounds) of waste. The vessel is sealed (venting through the condenser and subcooler) and shaft rotation is initiated. The vessel is then heated to a temperature of between 500 and 650°F and a vacuum is applied to the vessel. Specific temperatures, operating pressures, and desorption time will depend on the nature of the specific waste. Once the material has been heated for a specified time, the hot oil system is switched into a cooling mode and the material in the vessel is cooled for safe handling. The speed of the vessel agitator blade is then reduced and the discharge valve of the dryer is opened. The dried waste is then allowed to flow into a sealed receiving drum.

The vessel is heated by a gas-fired, hot oil system. When operating, the vessel temperature is monitored constantly, and hot oil flow is manually or automatically corrected in order to maintain the temperature within a specified range.

Overview of the Demonstration Test

Table II shows the three waste matrices were selected for the demonstration test.

Table II. Demonstration Test Feedstock Matrices

Batch Matrix	Total Batch Weight/ Volume (kgs/m ³)	Solids %	Organic content %	Moisture %	PCBs (mg/Kg)	Added Water (kg)	Added Diesel Fuel (kg)
Kaolin Sludge (Surrogate)	1,107/1.55	57	18	25	100,000	181	0
Sandy Soil (Surrogate)	1,660/1.70	71	10	19	20,000	200	109
Soil and Sediment (actual waste)	1,616/1.70	64	18.1	18	100,000	0	0

EPA and M&EC mutually considered these three matrices to be representative of the types of waste that would be likely candidates for treatment by VTD. The surrogate material for the first two batches consisted of virgin clay and sand obtained from a local distributor. The third batch consisted of actual waste generated by remediation activities at the DOE Oak Ridge Reservation.

Each demonstration run lasted over 100 hours total duration and involved several heat up/hold/cool down cycles. A vacuum of 711 to 737 mm (28-29") Hg was applied for the duration of each test run. In-process samples were collected at the bottom of each cool down

cycle and analyzed for total PCBs. A run was considered successful if total PCB concentration in the solid matrix was below 2 mg/kg. In-process samples were analyzed by MCL Laboratories, Inc. with confirmatory analysis performed by Lionville Laboratories, Inc using EPA Method 8082/3550B.

Emissions monitoring was required for each of the three test runs as follows:

- CO₂ and O₂ – EPA Method 3A
- CO – EPA Method 10
- Particulate/HCl/CL₂ – EPA Method 26A (Note: this was only required for a single 4-hr test run)
- SVOC – EPA Method 0010
- PCB/polychlorinated dibenzodioxins (PCDD)/polychlorinated dibenzofurans (PCDF) – EPA Method 0010 and Method 23

Velocity and temperature measurements for maintaining isokinetic flow were measured continuously with a single Pitot tube. All emissions monitoring was conducted from a single point that was downstream of the condenser, vacuum adsorber, and granular activated carbon (GAC) canisters. A complete Quality Assurance Project Plan consisting of sampling procedures, equipment calibration procedures, field blanks, sample preservation, and chain of custody procedures was provided to and approved by EPA prior to the start of the demonstration test.

The first demonstration run was approximately 104 hours in duration, and consisted of six discrete heat up/hold/cool down cycles. (See Figure 3)

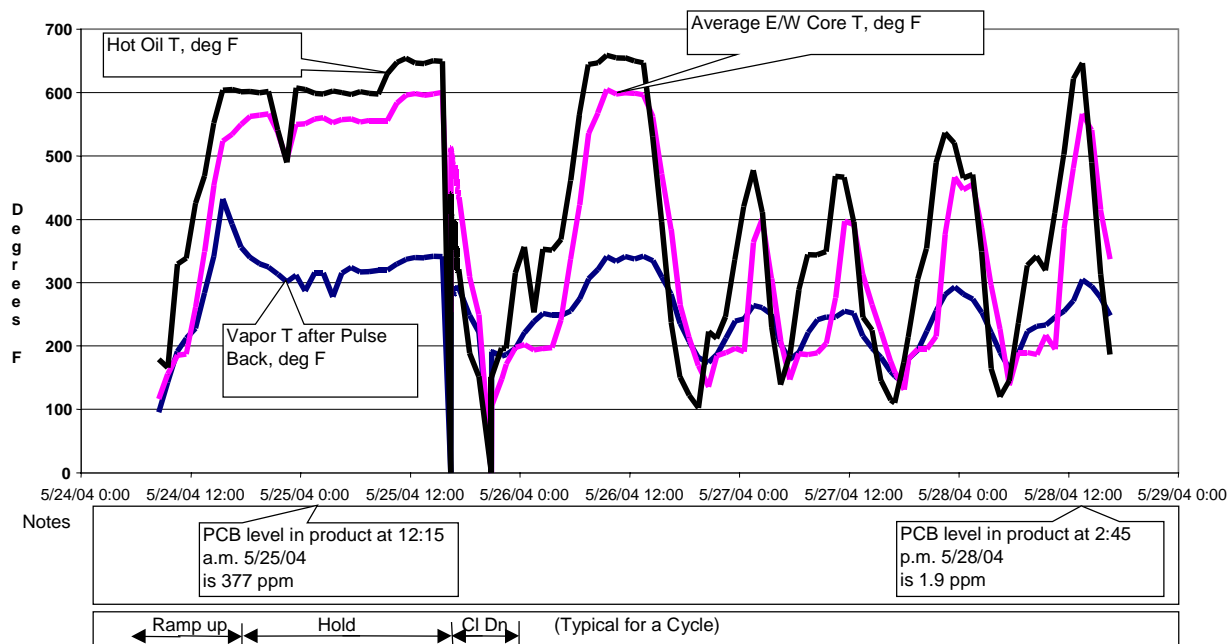


Fig. 3. Run 1 Treatment Chronology.[3]

The graph shows the temperature trends throughout each of the heat up/cool down cycles. In general, the temperature of the hot oil heat source always exceeds the desorber core temperature during heat up and reverses during cool down. Heat loss in the vapor line and the addition of purge nitrogen are limiting factors in the maximum vapor temperature achieved. The first sampling event was performed approximately 12 hours into the first cycle and showed that the total PCB concentration had dropped from 100,000 mg/kg to 377 mg/kg (or ppmw). It took over 90 hours to reduce the concentration from 377 mg/kg to <2 mg/kg.

There were no anomalies that occurred during this run other than a higher than expected number of heat up/cool down cycles required to reach the required level. This is likely due to the fact that the PCB molecules were tightly bound to the Kaolin clay particles.

The second demonstration run was approximately 52 hours in duration, and consisted of three discrete heat up/hold/cool down cycles. (See Figure 4)

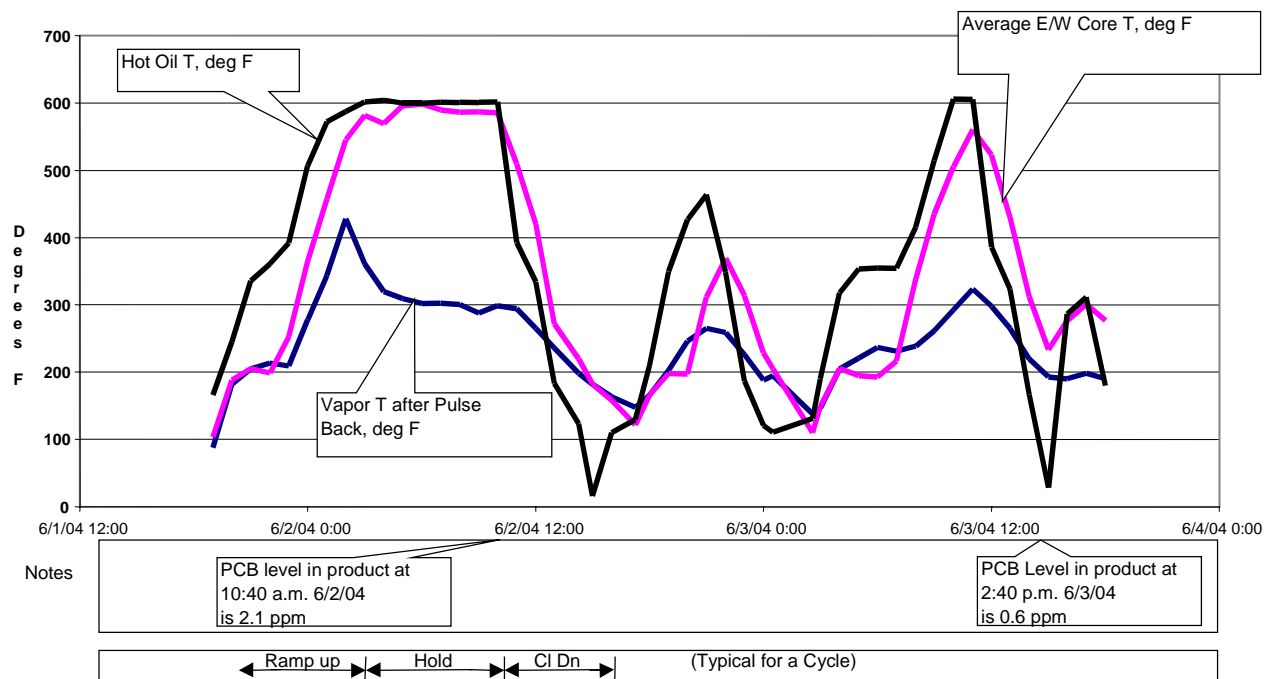


Fig. 4. Run 2 Treatment Chronology.[4]

As with the first run, a predictable temperature trend occurred throughout each cycle with the core temperature lagging behind the hot oil temperature during heat up and then reversing during cool down. The first sampling event was performed approximately 18 hours into the first cycle and showed that the total PCB concentration had dropped from 20,000 mg/kg to 2.1 mg/kg (or ppmw). It took approximately 34 hrs to reduce the concentration from 2.1 mg/kg to <2 mg/kg.

A process anomaly occurred during the first cycle of this run. A rupture disk opened on the positive pressure side of the vacuum pump. EPA's immediate concern was whether air entered the sample pipe and diluted the sample. If this were the case, the entire run would be disqualified because the air sample data would be invalid. The following drawing (Figure 5)

illustrates the desorber off-gas flow and the location of the rupture disk in relation to the sampling point:

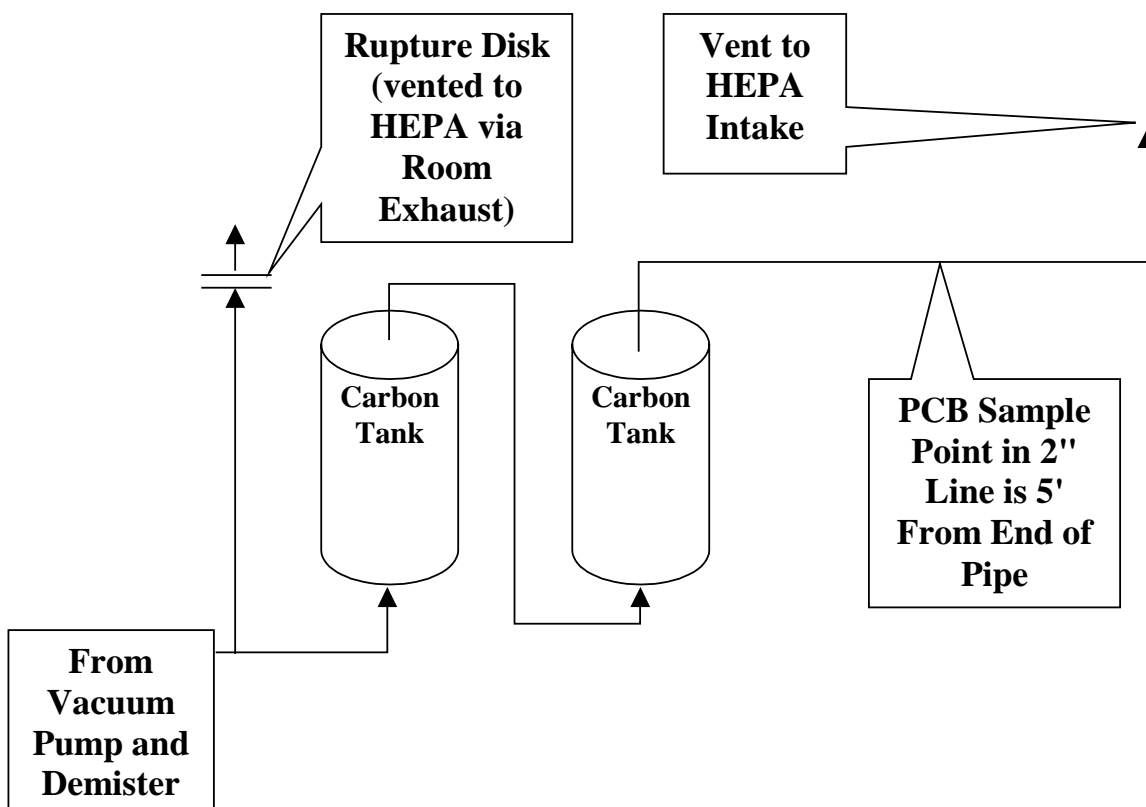


Fig. 5. Off-gas flow and sampling points. [5]

As shown in the drawing, the off-gas flow splits upstream of the rupture disk and the sampling point. There was no introduction of fresh air into the system as a result of the disk failure. Although the velocity of the slipstream was reduced for the period of time the disk was open, EPA agreed that the rupture disk opening did not invalidate the monitoring data.

The third demonstration run was approximately 196 hours in duration, and consisted of ten discrete heat up/hold/cool down cycles. (Figure 6)

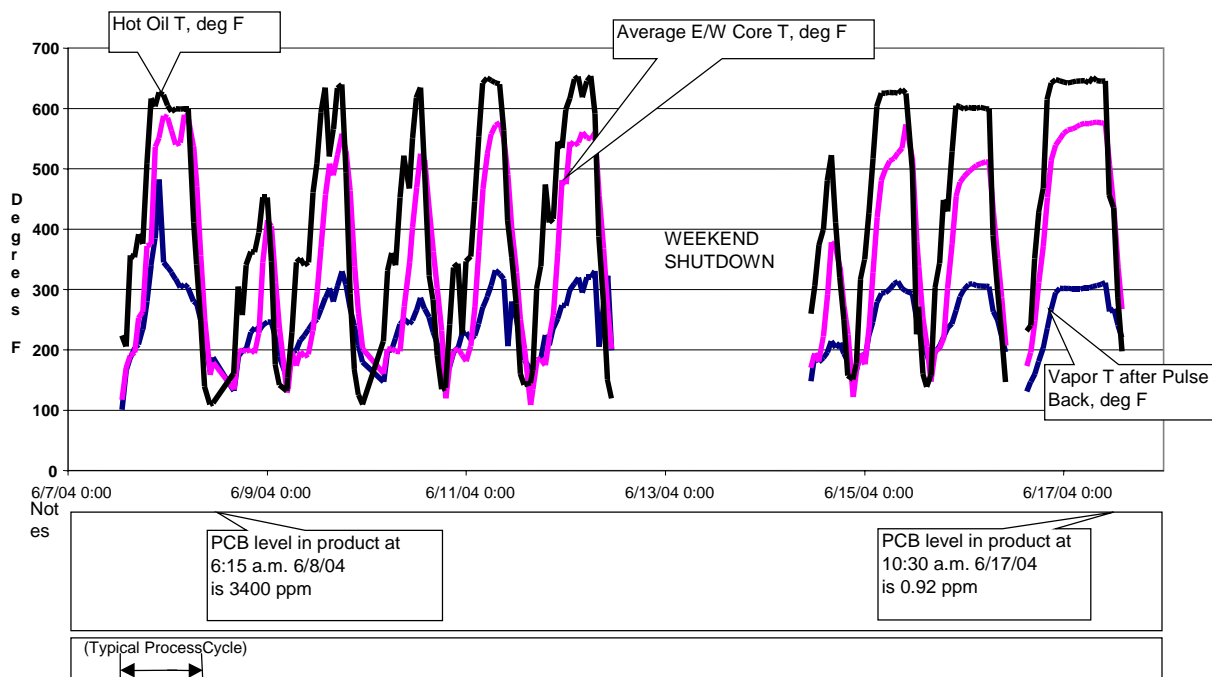


Fig.6. Run 3 Treatment Chronology.[6]

This run was split into two treatment periods due to a weekend shut down. As with the first two runs, there was an evident trend of the core temperature lagging behind the hot oil temperature during heat up and then reversing during cool down. The first sampling event was performed approximately 18 hours into the first cycle and showed that the total PCB concentration had dropped from 100,000 mg/kg to 3,400 mg/kg (or ppmw). It took approximately 175 hrs to reduce the concentration from 3,400 mg/kg to <2 mg/kg. This was an operational decision based on the assumption that this matrix, which was native clayey soil, would have a tendency to bind the PCB molecules.

The emissions monitoring results are shown in Table III.

Table III. Summary of Emissions Monitoring Results

Run	PCB DRE	PCB in solid matrix (ppmw)	2,3,7,8-TCDD TEQ (ng/dscm)	HCl + Cl ₂ (lb/hr)
1	99.9999990%	1.9	<0.011	NA
2	99.9999934%	0.60	<0.040	NA
3	99.9999975%	0.92	<0.100	0.51
Requirement to Pass	≥ 99.9999%	<2	<0.41	4.0
Result	Pass	Pass	Pass	Pass

CONCLUSION

Based on the test results, EPA Region IV issued an Interim Operating Permit on November 22, 2004. While in interim status, M&EC may treat PCB remediation was that has a feedstock concentration up to 20,000 mg/kg. M&EC is currently utilizing the VTD technology to treat PCB-contaminated soil and sludge generated by DOE. As a condition for granting interim operation status, EPA required that the rupture disk be replaced with a disk rated for a higher burst pressure (2 psig vs. 1.5 psig). Additionally, M&EC was required to outfit the rupture disk with a sensor that activates an alarm in the control room whenever the rupture disk opens. These two requirements were completed during the second week of November.

Vacuum thermal desorption has proven to be a viable treatment option for a variety of solid matrices that are contaminated with PCBs and other regulated organics. It is easy to make the argument that this is one of the most reliable PCB waste treatment methods available because there is no limit to the number of treatment cycles that can be performed on a waste stream, and the emissions potential is still extremely low, regardless of feedstock concentration. Volume increase is relatively low, depending upon the amount of water and solvent added during the treatment process, however the total disposal cost to dispose of the solid and liquid phases separately is significantly less than the cost of incinerating the untreated solid phase- which is currently the only alternative.

REFERENCES

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4. Ibid.
5. Ibid.
6. Ibid.