

Demonstration Testing of a Thermal Desorption Unit to Receive and Treat Waste with Unlimited Concentration of PCBs – 13437

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ABSTRACT

For the last nine years, EnergySolutions and TD*X Associates LP have teamed up to provide the most comprehensive organic removal treatment process in the radioactive waste industry. The high performance thermal desorption unit (HP-TDU) located at the EnergySolutions Clive facility in Utah has successfully processed over 1,850 tons of organically contaminated radioactive mixed waste. Products from the HP-TDU system include a radioactively contaminated dry solid material that can be disposed in the on-site landfill and an organic condensate with high thermal energy content that is generally below background radiation and capable of free-release to a non-radioactive incinerator. Over the years, Permits and approvals have been obtained through the state of Utah, United States Environmental Protection Agency (USEPA) Region 8, and USEPA headquarters that enable the treatment of several waste categories including volatile and semi-volatile organic compounds, combustion-coded (CMBST) compounds, volatile metals, and polychlorinated biphenyls (PCBs). The unit has recently successfully completed Demonstration Testing for PCB concentrations up to 656,000 ppm (parts per million). Solid processed material from this Demonstration Testing was less than two ppm PCBs in three separate treatment runs; reprocessing or additional treatment was not needed to meet this limit. Through post-demonstration permitting, the system is unlimited in scope as approval has been given to receive and solidify up to pure PCBs down to this processing limit concentration to complete treatment of mixed waste.

INTRODUCTION

Necessity for Technology

Few options are available to waste generators who create PCB-contaminated wastes. These options are diminished further if the waste also is radioactively contaminated. Federal PCB regulations [1] generally require incineration for PCBs in a liquid state. Hazardous waste treatment regulations [2] also require PCBs to be treated below its Universal Treatment Standard (UTS) of 10 mg/kg if present in a characteristically hazardous waste (a waste that contains ignitable, corrosive, reactive, or toxic D-codes as described in the hazardous waste generation regulations [3]). Chemical treatment technologies (e.g., chemical oxidation or reduction) can only treat PCBs to the UTS when PCB concentrations are low in the waste. Incineration appears to be the only viable alternative. But, since the Department of Energy's Toxic Substance Control Act (TSCA) incinerator in Oak Ridge, Tennessee shut down two years ago, there is no incineration

option for radioactively contaminated waste. This leads to the necessity of a different technology to treat radioactively contaminated waste that also contains PCBs. Thermal desorption is uniquely different from incineration, but can, if designed and operated properly, provide PCB reductions in the waste equivalent to incineration.

Technology Description

The thermal desorption technology separates volatile contaminants from solid matrices by indirectly heating the contaminated material in a relatively inert atmosphere and condensing the resulting off-gas. Figure 1 provides a schematic block diagram of the thermal desorption process which consists of three major subsystems: a thermal separation system (dryer), an off-gas treatment train, and a condensate collection system.

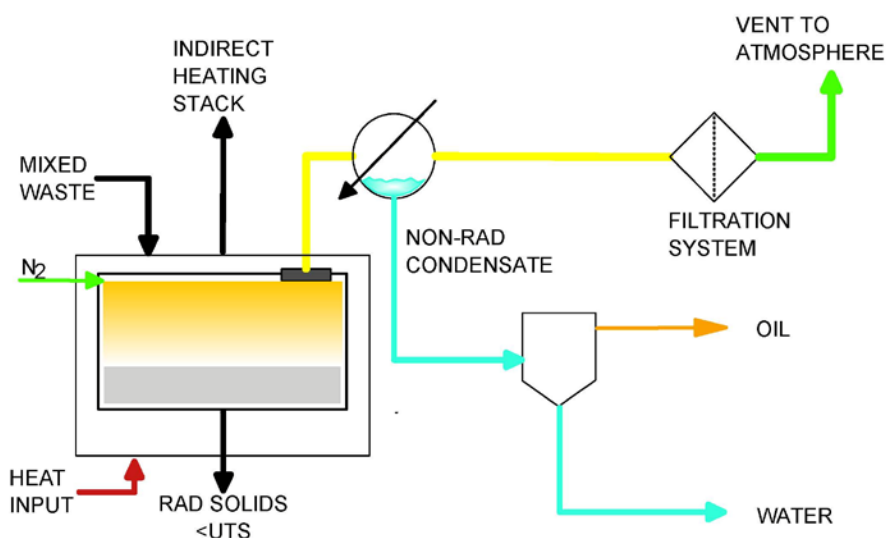


Figure 1. Thermal Desorption System Schematic Diagram

The dryer is a cylindrical vessel that is totally enclosed and indirectly heated by a separate propane fired furnace. Material within the dryer is never subject to an open flame. Further, the dryer at the EnergySolutions Clive Facility is kept under vacuum and is purged with a nitrogen carrier gas such that the atmosphere within the dryer has a reduced oxygen concentration (generally less than 6% during operation).

Waste (feed material) is introduced into the dryer through a feed hopper. The waste in the dryer is brought up to a predetermined temperature and then discharged as processed material. During

heating, lower boiling contaminants within the waste are volatilized and the off-gas is conveyed through a system of condensers and filters to remove the volatile contaminants from the off-gas prior to emission to the atmosphere. The condensate is collected for future management; typically incineration at a Resource Conservation and Recovery Act (RCRA) permitted facility, and contains minimal radioactivity, usually well below background levels. The processed material is a dry solid material that is below USEPA treatment standards for volatile contaminants and retains most of the radioactivity from the waste feed material.

The thermal desorption system employed at the Clive facility is the most advanced thermal desorption system constructed by TD*X. It has been specifically designed to meet the rigorous requirements necessary to process radioactively contaminated hazardous waste (mixed waste). To distinguish this unit from other units constructed by TD*X, it has been designated within the USEPA approval as the High Performance Thermal Desorption Unit (HP-TDU). A less robust system would not be capable of reaching the milestones described in this paper.

History

The HP-TDU was constructed early in 2003 and began treating mixed waste at the Clive facility through treatability studies and shakedown operations in late 2003. Previous Waste Management papers described the initial permitting process from a regulatory [4] and industry [5] viewpoint. Since that time, the HP-TDU has been extensively tested and proven capable to treat a large variety of wastes.

Successful demonstration testing of the HP-TDU was completed in August and September, 2004 with representatives from the State of Utah, USEPA Headquarters, and USEPA Region 8 present. This initial demonstration testing was performed for general volatile organic compounds, semi-volatile organic compounds, and PCBs in both a dry solid waste and in a wet sludge waste. The average PCB concentration treated during the demonstration testing was 6,888 ppm (parts per million). This concentration was listed as the feedstock limit in the USEPA national approval dated December 4, 2007.

Demonstration testing consisted of multiple treatment runs (batches) processed through the HP-TDU with samples collected of the feed and all exit streams, including the solid processed material, the liquid condensate, and the exhaust gas. Success was determined through a calculation of the removal efficiency (i.e., amount of contaminant in the feed compared to that in the off-gas), treatment of the processed material (below regulatory and prescribed standards), and an examination of detected compounds in all input/output streams.

The HP-TDU has been successfully demonstrated eight times, including the initial demonstration testing in 2004. Each of these demonstration tests added treatment capabilities to the HP-TDU.

These additional capabilities are described in a previous Waste Management paper [6] and include the ability to treat waste that carries the USEPA technology code of CMBST requiring combustion, and volatile metals such as mercury that requires the RMERC technology. Furthermore, since radioactivity within the feed waste remains in the solid and is negligibly transferred to the condensate, approval has been attained to “free-release” the condensate so that it may be incinerated at a permitted hazardous waste incinerator that does not have a Radioactive Material License.

With regard to PCBs, a demonstration test was performed in April, 2008 on shredded PCB capacitors to determine the applicability of the HP-TDU to both a debris-type matrix and a much higher concentration of PCBs. Based on the results of this demonstration test, a new USEPA national approval dated May 21, 2009 was received which amended and replaced the December 4, 2007 approval. This new approval maintained the 6,888 ppm PCB limit for most waste matrices, but allowed the treatment of shredded capacitors up to 162,733 ppm and also allowed those shredded capacitors to be blended down from a maximum concentration of 209,167 ppm in the initial waste.

PROCESS

Demonstration Testing Plan

The USEPA approval dated May 21, 2009 greatly increased the potential of the HP-TDU to treat PCBs; however, PCB concentration limitations remained. A new demonstration test was designed to remove these limitations. By mid-2009, discussions commenced between USEPA headquarters, USEPA Region 8, Utah regulators, *EnergySolutions*, and TD*X to devise a test that would demonstrate the full capabilities of the HP-TDU and allow PCBs at any concentration to be accepted and treated. USEPA representatives were skeptical of the plan as they had never experienced successful treatment at the PCB concentrations discussed, but allowed the demonstration process to continue.

The demonstration testing plan called for pure PCB liquid to be solidified in clean absorbent to obtain an extremely high PCB concentration solid. This solid was then to be fed into the HP-TDU and treated. The feed, processed material, condensate, and exhaust gas were all to be analyzed for PCBs. The exhaust gas was also to be analyzed for dioxins/furans and CEM (continuous emissions monitoring) for carbon monoxide, carbon dioxide, and oxygen.

Successful demonstration required that the following parameters be met:

- calculated PCB removal efficiency be greater than 99.9999% (six-nines);
- the PCB concentration in the treated solid processed material be less than two ppm; and

- dioxin/furan emissions be less than one nanogram per dry standard cubic meter (ng/dscm) of 2,3,7,8-TCDD TEQ (Toxic Equivalent).

The demonstration testing plan was submitted to USEPA headquarters and Region 8 on July 24, 2009. The plan described the following three-phase approach to demonstration testing:

1. A limited period (4-week) shakedown period to optimize the feed rate and processing parameters of the HP-TDU. During this shakedown period, feed waste was allowed to exceed the PCB concentration restrictions of the May 21, 2009 approval.
2. A one-run pre-test to be performed on high PCB concentration waste within the first five days of the shakedown period. The feed and exhaust would be measured for PCBs and removal efficiency (RE) established. Exhaust dioxin/furan and CEMs were also required to ensure emissions were protective of human health and the environment. As this was performed at the beginning of the shakedown period, the pre-test was not required to meet all of the demonstration testing objectives.
3. A three run demonstration test with all input and output streams analyzed for PCBs and the exhaust analyzed for PCBs, dioxins/furans, and CEMs.

The demonstration testing plan also contained a sampling and monitoring plan (with associated sampling matrices), project organization (including key individuals, laboratories, and contractors associated with the testing), and procedures for data calculations and reporting.

During these discussions, USEPA regulators made the decision that the HP-TDU should be permitted as a permanent unit by Region 8 as well as a mobile unit through national headquarters. This approval change began with the Demonstration Approval dated November 16, 2009 received from USEPA Region 8.

Shakedown and Pre-Test

The shakedown period began on November 16, 2009. The required pre-test was performed on November 18, 2009 with state and USEPA regulators in attendance. The pre-test consisted of a single batch of PCB contaminated waste with associated exhaust sampling for PCBs, dioxins/furans, and CEMs. Based on analytical data, the feed waste had a PCB concentration of 123,900 ppm. Results of the pre-test demonstrated a removal efficiency of eight-nines and a dioxin/furan TEQ concentration of 0.0029 ng/dscm. Both of these results were within testing objectives. The solid processed material had a detectable PCB concentration of 13.8 ppm, above the testing objective of two ppm; however, it was not necessary to meet that objective at this time.

The process was optimized through continued shakedown operations in December, 2009 through March, 2010. Continual improvements in the system and operations were made during this shakedown period, preparing the HP-TDU for Demonstration Testing.

Demonstration Testing

Demonstration testing began on March 30, 2010 (the test on March 30, 2010 was scrubbed thanks to several power failures at the facility on that day). Due to exhaust sampling errors briefly discussed below, five treatment runs were necessary to complete the testing. The five treatment runs were performed on March 31, 2010; April 1 and 2, 2010; and July 27 and 28, 2010.

PCBs for the feed were collected from PCB large capacitors received previously at the Clive facility. Prior to the demonstration testing event, the PCB large capacitors were punctured and drained into containers. Seven drums of PCB liquid from PCB large capacitors was created in this manner. A composite sample was collected from the liquid within the drums and analyzed for PCBs. The resulting concentration of this analysis came up greater than 1,000,000 ppm due to the extremely high dilution necessary for the laboratory to analyze the sample. For all future calculations, the PCB liquid was assumed to be pure PCBs (1,000,000 ppm).

The PCBs were kept in liquid form until the day before demonstration testing. With state and USEPA regulators watching, the liquid was poured into absorbent and the mixture stirred to obtain high PCB concentration feed drums for demonstration testing. Each drum was then sealed and transported to the HP-TDU operations building for treatment. During the solidification process, a sample was collected of the oil used in creating each waste feed drum.

In addition to demonstrating the HP-TDU for high concentration PCB, the test was also used as the RCRA permit-required biennial demonstration testing of the unit. For this additional test, it was necessary to add spike compounds to the feed in order to demonstrate the ability of the HP-TDU to effectively treat volatile and semi-volatile organics. As such, a separate spike feed drum was created each day of testing. These spike drums consisted of reagent grade purchased chemicals mixed with clean absorbent. Spike chemicals included trichloroethylene, 1,2-dichlorobenzene, trans-1,2-dichloroethene, and p-cresol. These compounds were spiked into the first three treatment runs at concentrations of 7,000-10,000 ppm each.

Feed each day consisted of clean sand as a base in the dryer, one drum of the solidified PCB liquid, and one drum of the absorbed spike compounds. During each treatment run, internal pressure in the dryer was maintained below atmospheric at pressures between 330 and 700 mmHg. Oxygen in the dryer was maintained below 3% for a majority of the treatment process.

For each treatment run of demonstration testing, samples were collected from the feed, the solid processed material, the liquid condensate, and the exhaust gas. The feed samples were composites from both the top and the bottom of each drum as it was being fed into the feed hopper of the HP-TDU. Processed material samples were collected by opening a port in the discharge hopper while the material was cooling. Several aliquots were collected from various portions of the processed material and composited into a single sample. Liquid condensate samples were collected from the drain line as the condensate was transferred into a tote container for storage. Condensate generally has both an aqueous and a non-aqueous portion. For a conservative estimate of organics in the condensate, only the non-aqueous portion was sampled during the demonstration testing. State regulators collected splits of all solid and liquid samples collected.

Exhaust sampling consisted of two separate events: chemical sampling by experienced emission test contractors and radiological sampling by EnergySolutions Health Physics personnel. Exhaust chemical sampling was collected through a specially designed manifold located outside the radiological controlled area. The emission test contractors used USEPA methods to collect samples for volatile organic compounds, semi-volatile organic compounds, PCBs, dioxins/furans, hydrochloric acid and chlorine gas, particulate matter, metals, and CEMs for carbon monoxide, carbon dioxide, and oxygen. Many of these tests were required for the permit-required biennial demonstration test and not for the higher concentration PCBs. Radiological samples were taken on several media to ensure radioactivity was not being emitted through the exhaust. Radiological samples were collected on paper filters, charcoal filters, silica gel, and gas (marinelli jars).

Method-required isokinetic sampling rates were not obtained by the emission test contractors for dioxins/furans on the March 31, 2010 treatment run. Since this parameter was critical to the USEPA approval process and since the results of the test could not be confirmed, regulators invalidated the results of that treatment run. Although the tests were considered invalid, analytical results were obtained since the results would be biased high based on the sampling issue. The results came back showing that the dioxin/furan requirement was met for this treatment run.

Another issue associated with the emission test contractors occurred on the April 2, 2010 treatment run. When the glass nozzle used for collecting the isokinetic dioxin/furan sample was removed from the manifold, it appeared to be rotated approximately 110 degrees from the direction of the flow. Regulators invalidated this test as they could not certify that the proper amount of sample was collected.

Scheduling conflicts and availability of required sampling media caused the remainder of the demonstration testing be delayed several months. Regulators re-convened at the Clive Facility on July 27 and 28, 2010 to complete the two treatment runs that had previously been invalidated. Since there were no problems in the previous tests with the volatile and semi-volatile organic samples, it was not necessary to add the spike compounds during these last two treatment runs.

Furthermore, the only exhaust gas chemical tests needed for these treatment runs was PCBs, dioxins/furans, and metals. These last two treatment runs were successfully completed with no further incidents.

Results and Discussion

Results of PCB analyses in all solid and liquid samples collected during Demonstration Testing are provided in Table I. Because of the extremely high dilution necessary, many of the laboratory analyses had results greater than 1,000,000 ppm. As this result is impossible, these results are considered to be 1,000,000 ppm for all future calculations. The results in Table I show an average PCB Feed concentration of approximately 837,700 ppm for the five treatment runs during demonstration testing. The pre-test had results greater than two ppm for the solid processed material; however, after refinements were made to the system, all demonstration testing PCB results were non-detectable; well below the required objective of two ppm.

TABLE I. PCB Solid Sampling Results

	Pre-Test	3/31/2010	4/1/2010	4/2/10	7/27/2010	7/28/2010
PCB Oil	NA	1,000,000 ^a	1,000,000 ^a	1,000,000 ^a	1,000,000 ^a	870,000
Waste Feed	123,900	696,500	863,000	765,000	1,000,000 ^a	864,000
Condensate	510,400	1,000,000 ^a	1,000,000 ^a	974,000	5,179	647,600
Processed Material	13.8	U (0.0997)	U (0.0985)	U (0.0903)	U (0.481)	U (0.463)

^a Results greater than 1,000,000 ppm have been assumed equal to 1,000,000 ppm.

Because of the high concentration of PCBs used for this demonstration testing, feed concentration analytical results could not be relied upon for further calculations. A more reliable way to calculate the feed concentration of PCBs is to use the oil analysis (demonstrating in all but one case that the PCBs were pure; 1,000,000 ppm) and use a mass balance to calculate the concentration of PCBs within the feed waste. The weights of oil and absorbent were recorded at the time the waste feed drum was created. Table II shows all the weights used during this process, and the final PCB feed concentration calculated using these weights.

TABLE II. PCB Weight Mix Ratio – Feed Concentration

	3/31/2010	4/1/2010	4/2/2010	7/27/2010	7/28/2010
PCB Oil (ppm)	1,000,000	1,000,000	1,000,000	1,000,000	870,000
PCB Oil (lb)	363	453	525	641	272
Absorbent (lb)	225	225	225	225	225
Total Wt. (lb)	588	678	750	866	422
PCB Conc (ppm)	617,000	668,000	700,000	740,000	561,000

As an example of the final PCB feed concentration calculation, for the 3/31/2010 treatment run 363 lbs of oil was added to 225 lbs of absorbent for a total weight of 588 lbs of feed waste. Since the analyzed PCB concentration of the oil was greater than 1,000,000 ppm, the waste was assumed to be pure PCB oil and the calculated feed waste concentration is $(363/588) \times (1,000,000/1,000,000) = 617,347$ ppm which is rounded to 617,000 ppm in the table.

The removal efficiency (RE) for PCBs is calculated using the following equation:

$$RE (\%) = 100 \times \frac{\text{PCB Emission Rate}}{\text{PCB Feed Rate}} \quad (\text{Equation 1})$$

All of the information necessary to calculate removal efficiencies in each demonstration test run is tabulated in Table III. The PCB Emission Rate is calculated from the analysis of the exhaust sample and the sampling rate. This information was provided by the emission test contractor in their final report to EnergySolutions.

TABLE III. PCB Removal Efficiencies

	Pre-Test	3/31/2010	4/1/2010	4/2/2010	7/27/2010	7/28/2010
PCB Feed Conc. (ppm)	123,900	617,000	668,000	700,000	740,000	561,000
PCB Feed Wt (lb)	NA	586	578	750	786	434
Total Feed Wt (lb)	NA	2,504	2,514	2,562	2,712	2,332
Dryer Feed Rate (lb/hr)	294	608	692	603	651	636
PCB Feed Rate (lb/hr)	34.8	87.8	106.3	123.5	139.6	66.4
PCB Emission Rate (lb/hr)	8.45E-8	2.42E-7	6.36E-7	1.90E-6	5.75E-7	3.65E-7
Removal Efficiency (%)	99.9999998	99.9999997	99.9999994	99.999999	99.9999996	99.9999995

The PCB Feed Rate is calculated through several parameters collected during each demonstration test and provided in Table III. The PCB Feed Concentration is taken from Table II. Each container fed into the HP-TDU was weighted before and after feeding to get an accurate weight of the amount of material fed into the dryer. The PCB Feed Weight is the weight of the waste fed into the HP-TDU. The Total Feed Weight includes the PCB waste, the sand base, and the spike drum (if applicable). The dryer feed rate is calculated by the HP-TDU operators as the total

weight fed divided by the total batch treatment time. These values are used to calculate the PCB feed rates shown in the table.

Once the feed rate and emission rate are established, Equation 1 is used to calculate the removal efficiency. All calculated removal efficiencies for this demonstration test are at least 99.999999% (eight-nines), exceeding the demonstration requirement of at least 99.99999%.

The third requirement for successful demonstration testing is related to dioxin/furan concentrations in the exhaust gas. The USEPA has established that the carcinogenic risks of dioxins and furans in an exhaust stream is attained by equating each specific dioxin or furan to the most toxic variety, 2,3,7,8-tetrachlorodibenzo-p-dioxin or TCDD. This procedure is known as finding the toxic equivalent, or TEQ of the dioxins and furans in the exhaust stream. To perform this calculation, the USEPA has provided risk guidance on toxic equivalent factors (TEFs) for each individual dioxin and furan as their carcinogenicity relates to 2,3,7,8-TCDD. Table IV lists the calculated 2,3,7,8-TCDD TEQs for each of the applicable demonstration testing treatment runs (note that the dioxins/furan testing was invalidated by regulators on the 3/31/2010 and 4/2/2010 treatment runs).

The TEQ concentrations shown in Table IV are 20 to 600 times lower than the limit of 1.0 ng/dscm required for successful demonstration testing.

TABLE IV. Dioxin/Furan TEQ Analysis

	Pre-Test	4/1/2010	7/27/2010	7/28/2010	Average
Total 2,3,7,8-TCDD TEQ (ng/dscm)	0.0029	0.0016	0.0354	0.0537	0.0302

The results in table's I-IV were submitted to USEPA Region 8 and USEPA headquarters in a report dated December 1, 2010. The report clearly represented the waste as pure PCBs prior to processing for the HP-TDU. Based on this information, and discussions between EnergySolutions, TD*X, and regulators, a final approval from USEPA Region 8 was received on September 16, 2011. This final approval allowed feed concentrations of PCBs up to 656,000 ppm (the average demonstrated in this test) regardless of the waste matrix. Furthermore, the approval allowed incoming PCB concentrations to be unlimited as long as they are blended down to this feed concentration prior to treatment through the HP-TDU.

CONCLUSIONS

The evolution of PCB treatment through the HP-TDU located at the EnergySolutions Clive Mixed Waste Facility is shown in Table V. Through continual successful operations and demonstrations, the HP-TDU is now able to process PCBs up to 656,000 ppm, and the Clive facility is now approved to accept any concentration of PCBs for treatment through the HP-TDU.

Table V. Evolution of PCB Treatment at Clive

USEPA Approval Date	Maximum PCB Concentration for Treatment	Maximum Incoming Waste PCB Concentration	Notes
12/4/2007	6,888 ppm	6,888 ppm	Only for soils and sludges
5/21/2009	6,888 ppm	6,888 ppm	Only for soils and sludges
	162,733 ppm	209,167 ppm	Shredded PCB Capacitors
9/16/2011	656,000 ppm	1,000,000 ppm	No limits on concentration or matrix

Furthermore, the feed material has essentially no limit on metal or organic concentrations because of the unit’s demonstrated high efficiency for metals and organics control. The unit does have a limit for mercury mass per batch, but that is quite manageable with the waste materials requested for treatment. The combination of unrestricted PCB, RCRA organic compounds, and unrestricted toxic metals content provides unique benefits to the management of complex mixed waste materials.

The demonstration testing in 2010 over exceeded regulator’s expectations and proved that the HP-TDU designed by TD*X is the most robust thermal desorption system available. This approval, along with other approvals to treat combustion-coded waste and other contaminants at any concentration makes this unit invaluable for cleaning up legacy wastes which, until this approval was received, were orphan wastes with no foreseeable outlet.

REFERENCES

1. Code of Federal Regulations (CFR), Title 40, Protection of Environment, Part 761, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions
2. Code of Federal Regulations (CFR), Title 40, Protection of Environment, Part 268, Land Disposal Restrictions
3. Code of Federal Regulations (CFR), Title 40, Protection of Environment, Part 261, Identification and Listing of Hazardous Waste, Subpart C, Characteristics of Hazardous Waste
4. Lukes, G. and Willoughby, O., “Permitting and Testing of a Vacuum Thermal Desorption Unit for Treating Mixed Waste at the Envirocare of Utah, Inc. Mixed Waste Facility Located at Clive, Utah”, Waste Management 2005, February 27-March 3, 2005, Tucson, AZ

5. Orton, T., “RCRA Permitting of a Vacuum Thermal Desorption System”, Waste Management 2005, February 27-March 3, 2005, Tucson, AZ
6. Orton, T. “Increased Capabilities of Thermal Desorption”, Waste Management 2009, March 1-5, 2009, Phoenix, AZ