

Air Emissions Sampling from Vacuum Thermal Desorption for Mixed Wastes Designated with a Combustion Treatment Code for the EnergySolutions LLC Mixed Waste Facility - 9099

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ABSTRACT

EnergySolutions LLC is permitted by the State of Utah to treat organically-contaminated Mixed Waste by a vacuum thermal desorption (VTD) treatment process at its Clive, Utah treatment, storage, and disposal facility. The VTD process separates organics from organically-contaminated waste by heating the material in an inert atmosphere, and captures them as concentrated liquid by condensation. The majority of the radioactive materials present in the feed to the VTD are retained with the treated solids; the recovered aqueous and organic condensates are not radioactive. This is generally true when the radioactivity is present in solid form such as inorganic salts, metals or metallic oxides. The exception is when volatile radioactive materials are present such as radon gas, tritium, or carbon-14 organic chemicals. Volatile radioactive materials are a small fraction of the feed material.

On August 28, 2006, EnergySolutions submitted a request to the USEPA for a variance to the Land Disposal Restrictions (LDR) standards for wastes designated with the combustion treatment code (CMBST). The final rule granting a site specific treatment variance was effective June 13, 2008. This variance is an alternative treatment standard to treatment by CMBST required for these wastes under USEPA's rules.

The State of Utah provides oversight of the VTD processing operations. A demonstration test for treating CMBST-coded wastes was performed on April 29, 2008 through May 1, 2008. Three separate process cycles were conducted during this test. Both solid/liquid samples and emission samples were collected each day during the demonstration test. To adequately challenge the unit, feed material was spiked with trichloroethylene, o-cresol, dibenzofuran, and coal tar.

Emission testing was conducted by EnergySolutions' emissions test contractor and sampling for radioactivity within the off-gas was completed by EnergySolutions' Health Physics department. This report discusses the emission testing procedures and the results of emission samples in the exhaust gas of the VTD unit. Combustion parameters (i.e. carbon monoxide, carbon dioxide, and oxygen) were monitored as indicators of process operation. The emission rates of volatile, semi-volatile, hydrochloric acid, and radiological gases are low and in compliance with applicable emission limitations. Regulatory review of the data is ongoing but preliminary reviews indicate that the processed material meets LDR standards and the emissions meet permit conditions.

INTRODUCTION

Demonstration testing for treating CMBST-coded wastes was performed on April 29, 2008 through May 1, 2008. The purpose of the air emissions sampling program was to measure the mass emission rate, from each of the three tests, to the atmosphere. Data from this sampling program is to be used in conjunction with operations data and other sampling data from the feed-, process material, and condensate to demonstrate effectiveness of the treatment for CMBST-coded wastes and compliance with their state-issued Part B Permit.

CMBST-coded wastes are organically contaminated wastes that contain hazardous waste codes “P” and “U,” and that require CMBST as the LDR treatment standard. Under 40 CFR Section 268.42, “CMBST” is defined as “[h]igh temperature organic destruction technologies, such as combustion in incinerators, boilers, or industrial furnaces operated in accordance with the applicable requirements of 40 CFR Part 264, Subpart O, or 40 CFR Part 265, Subpart O, or 40 CFR Part 266, Subpart H, and in other units operated in accordance with applicable technical operating requirements; and certain non-combustive technologies, such as the Catalytic Extraction Process.”¹

Three parameter groups were measured during demonstration testing: volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and hydrochloric acid (HCl). Three continuous emission monitoring (CEMs) parameters were also measured during demonstration testing: carbon monoxide (CO), carbon dioxide (CO₂), and oxygen (O₂).

SAMPLING STRATEGY

For purposes of collecting off-gas samples, a sample train was set-up within the VTD process vent line (See Figure 1). The sample train consists of a sample manifold constructed specifically for this purpose and applicable flow measurement devices.

The sample train was located within the process vent line after all off-gas treatment equipment (condensers and filters) and before the blower at the process vent stack. Sampling from this point provides an accurate picture of the gases that are emitted to the atmosphere from the VTD unit.

The dry-gas meter located at the beginning of the sampling train is necessary to calibrate the vent flow meter (rotameter) prior to the test. The point after the sampling manifold labeled “Radiation” is where the radiological sampling is performed (filters, etc.).

Table 3 describes sampling and analytical procedures used to collect the necessary samples.

SAMPLING AND ANALYSIS PROCEDURES

Descriptions of the test methods used for sampling are described here. Process gas flow characteristics were measured and calculated using the procedures and calculations described in EPA Reference Methods 1a and 2d, (sample location and velocity measurement, respectively). The Method 1a sample port location was modified by using only one sample point in the center of the manifold. This modification was necessary to reduce the possibility of breaking the glass nozzles required for these test methods and to reduce air leakage into the sampling manifold during the process of moving the sampling nozzle from one sample point to another. A broken nozzle would void the results of the entire test. Since the manifold was only four inches in diameter and the sampling nozzles are one inch to one and one-eighth inches in diameter, the risk of accidentally jamming the glass nozzle into the steel wall of the manifold when attempting to reposition the nozzle was great. Moreover, the sampling traverses required in EPA Method 1a were not necessary in this situation to obtain accurate results for the following reasons:

First, the sampling manifold is an unusual case in that it has a very small diameter of only four-inches and an extremely slow gas velocity of approximately 1.9 to 4.0 feet per second. The typical stack diameter for this method is greater than three feet and the typical gas velocity for this method is 50 feet per second. In order to maintain isokinetic sampling rates and obtain a sample of sufficient volume, unusually large diameter sample nozzles were required.

¹ EPA has not established any analytical method to determine the concentration levels for all organic constituents that are assigned P and U hazardous waste codes. As a result, EPA promulgated the incineration (CMBST) method of treatment as the treatment standard for these difficult to analyze P and U hazardous waste codes.

A typical nozzle size for EPA Method 1a is one-eighth to one-quarter inch in diameter. Due to the low flow rate through the VTD process vent sampling manifold, the nozzles needed to be one inch to one and one-eighth inches in diameter. For a four-inch duct, the Method 1a language requires locating four points across a sampling traverse at distances of 0.25, 1, 3, and 3.75 inches from the duct wall. However, Method 1a specifies that traverse points should not be located any closer to the duct wall than the inside diameter of the nozzle. For a one inch diameter nozzle, this eliminates the required standard location for all four traverse points and leaves two sample points located at 1.5 and 2.5 inches into the duct. One sample point located at the midpoint of the manifold (two inches from the walls) would encompass both of these specified sample locations within the diameter of the nozzle. Therefore, sampling conducted at the midpoint of the manifold included the desired traverses required by EPA Method 1a.

Second, in a typical EPA Method 1a sampling situation the nozzle area is very small when compared to the flow area of the stack. For example a one-quarter inch nozzle used in a three-foot diameter stack gives a ratio of 0.0048 percent. This means that the actual sample collected is only 0.0048 percent of the gas exiting the stack. Since the sample volume is so small as compared to the exhaust gas volume it is important to sample at points that will give an accurate representation of the full cross section of the stack. However, for the VTD off-gas sampling campaign, because the nozzles were large and the manifold diameter was small, the ratio of nozzle area to flow area is 7.6 percent. This large sample to exhaust gas ratio makes the exact location of the sampling points less critical in obtaining a representative sample.

Third, the most important component of the multiple point traverses in a typical EPA Method 1a test is to get an accurate measurement of the average gas velocity across the flow area. This is done by using a pitot tube attached to the sampling probe. In a large stack, the gas velocity can vary greatly across the cross-section of the flow area. The gas velocity directly effects the calculation of the stack gas flow rate and the emission rate in lbs/hr so an accurate measure of the average gas velocity within the flow area is critical to the test results. However, for the VTD off-gas sampling campaign, the total gas flow rate was measured directly using a rotameter as per EPA Method 2d (the entire gas stream directed through the rotameter). Therefore, eliminating the sampling traverses had no effect on the accuracy of the measurement of gas flow rate.

Lastly, other than the gas velocity measurement mentioned above, the reason for a sampling traverse is to measure an average pollutant concentration in stacks where centrifugal forces cause solid or liquid particles to stratify to one side of the stack. This is expected; for example, at the outlet of a centrifugal fan. Since this phenomenon is based on centrifugal force, it occurs with large particles and high gas velocities. In the extremely low gas velocity of the VTD off-gas sampling manifold, the centrifugal force developed around turns was not large enough to stratify the particle concentration. For this process, design pollutant stratification is a concern only for solid or liquid particles; it has no affect at all on gaseous pollutants, as there is no mechanism to stratify gases in the system.

The design of the VTD unit is such that the exhaust gas flow of the system is very low. Even using the smallest duct diameter allowed by EPA Method 1a (i.e., four inches), the velocity of the gas is too low to measure with a pitot tube and standard pressure sensors. For situations in which sampling is performed in low gas velocity situations, the EPA has developed alternative methods to the typical pitot tube measurements of EPA Method 2. For this test, EPA Method 2d (rotameter) was used to determine the gas flow rate. A rotameter was installed just upstream of the sampling manifold. Prior to the initiation of sampling, the rotameter was calibrated using a calibrated dry-gas meter, as per EPA Method 2d. The rotameter measurement of total gas flow rate was used to calculate the emission rate for each of the measured pollutants.

Due to the low exhaust gas flow rate and that three emission sampling trains were operated simultaneously in series in the sampling manifold, the total volume of the sample gas extracted from the manifold was large enough to affect the gas velocity in the manifold. For purposes of sampling at isokinetic rates, the rotameter flow rate was adjusted for each of the sample port locations by subtracting the flow rate of the sample gas pulled from the manifold by each sampling train upstream of each sampling port. DMK developed a spreadsheet to calculate the sample extraction flow rate as measured by the EPA Method 2d rotameter. Each sampling train required to sample at an isokinetic rate, was operated to match the manifold gas velocity as calculated by the spreadsheet. Rotameter and manifold gas temperature readings were performed and the sample rates were adjusted to the calculated rates every five minutes. As a quality control check of the accuracy of the calculated gas flow rates from the spreadsheets, a second calibrated rotameter was installed at the end of the sampling manifold. Readings from the second rotameter were compared to the calculated flow rate after all sample volumes were subtracted. This method showed that the measured flow rate at the end of the sampling manifold and the calculated flow rate were within 10 percent.

EPA Method 3a (O₂ and CO₂) was performed without any modifications.

The continuous gas sample option of EPA Method 10 (CO) was used for Demonstration Testing. During each day's process cycle of waste through the VTD, the CO concentrations varied from relatively low to high concentrations. When the concentration approached the upper limit of the CO monitors measurement scale, a dilution system was used to measure the higher concentrations for the remaining portion of the test.

EPA Method 26a hydrogen halides (HCl) was modified by eliminating the two sodium hydroxide impingers. These impingers are used to collect halogens, which were not of interest during this test. In place of those two impingers, one empty impinger was used for the collection of moisture. Process cycles two and three used a fifth impinger of silica gel. This was used to confirm that no moisture was escaping the condenser system. All of the silica gel in the fourth impinger turned pink at the end of the first process cycle, so the second impinger was added for process cycles two and three. Silica gel turns pink when it has been spent. It has been surmised that the high levels of CO in the sample gas were responsible for the color change because all sample runs measured consistently low levels of moisture in the exhaust gas.

EPA Method 0030 (VOCs) was modified to measure VOCs because the length of the sampling time was unknown for each process cycle. The slow volatile organic sampling train option of section 1.1.4 of the method was used. The first five sorbent trap pairs were sampled for 40 minutes each. The sixth and last sorbent trap pair was sampled until the end of the process cycle.

EPA Method 0010 (SVOCs) for the measurement of polychlorinated biphenyls was used without any modification.

SAMPLING AND ANALYSIS RESULTS

Results of the sampling and analysis for the aforementioned parameters are shown in Table 1.

QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

In general, all sampling equipment and instrumentation was checked and routine maintenance performed prior to the demonstration testing.

Equipment Calibration and Maintenance

All chemical reagents used in sample recovery were reagent grade with appropriate laboratory certifications. The thermocouples were calibrated at multiple temperatures in a water bath and oven. The reference thermometers were calibrated by the manufacturer.

The emission test contractor's field barometer was calibrated by comparison to the U.S. Weather barometer at the Salt Lake Airport. The sample volume dry-gas meter and flow orifice were calibrated against a standard meter or set of critical orifices with calibration factors supplied by the manufacturer. A Post-test calibration was also be performed following each mobilization of equipment to the site.

Pre- and post-test leak checks were be performed on the sampling train and gas sampling lines. The results of these leak checks were recorded on field data sheets. All material such as glass nozzles and teflon ferules used in sampling trains were suitable for the temperature and purposes of the testing. The components were configured to avoid sample interference.

The vent flow meter rotameter in the process vent sampling manifold was calibrated prior to the commencement of Demonstration Testing. This calibration was performed in accordance with EPA Method 2b using the previously calibrated dry-gas meter. At least three different flow rates were used to form the calibration curves of the rotameter. These flow rates encompassed the flow regime expected during demonstration testing.

Sample Recovery Preparation

A separate room, free from blowing dust and other potential contaminants, was designated for setting up the necessary equipment for sample recovery. Equipment organized by test method include: pre-cleaned sample bottles, petri dishes, solvent rinses in squeeze bottles, and probe brushes. Sample bottles and petri dishes were pre-labeled. Transfers of custody forms were prepared before-hand for all samples and sample blanks.

Sample Blanks

One field blank (a complete setup, pre-test leak check, maintaining the train heated during sampling, post-test leak check, and disassembly of the train in the field) and one set of reagent blanks were taken for each test method. These blanks were packaged, shipped, and analyzed by the laboratory. No adjustments to the calculated emission rates were made as a result of the blanks.

Sample Ports

The demonstration test involved multiple sampling trains in series in a small diameter sampling manifold with a low flow rate, there was concern that leakage of gas from the space between the sampling probes and walls of the sampling ports could bias the test results. To prevent this problem, compression fittings with leak free seals were attached to the sample ports using the sample port's pipe threads. This formed a leak-free fitting for all sampling trains.

Sample Collection Temperature Controls

All sampling trains were equipped with automated temperature controllers on probe and filtration oven heaters in order to maintain the proper temperatures as specified in the test methods.

Data Validation

Computer spreadsheets were designed to store the field data and perform necessary calculations. These spreadsheets were audited prior to use in the field. The field data were entered separately into two independent spreadsheets and hard copy data sheets, and the resulting calculations of flow rates, meter volumes, and isokinetic flow rates compared. If any significant differences were found, the source of the difference was located to correct data entry or calculation errors.

SAMPLING AND ANALYSIS PROCEDURES FOR RADIONUCLIDES

The feed waste did not contain iodine, krypton, or tritium. Therefore, it was only necessary to monitor particulates in the off-gas. Sampling was conducted by taking a slip stream from the off-gas line after the sampling manifold and after the samples mentioned in the previous section. The slip stream pulled a steady flow through the particulate filter over the duration of each process cycle. The filters were counted onsite prior to sending them to an offsite laboratory for gamma spectroscopy analysis. The counting data of each filter prior to shipment to the offsite laboratory are provided in Table 6. The offsite laboratory analyzed the samples for thorium, radium, and total uranium. Very minimal detections were noted as provided in Table 2.

Table 1 Results of Air Emission Sampling for Non-Rad

Parameter	CMBST-1 Test	CMBST-2 Test	CMBST-3 Test	Average	Regulatory Limit	Units
Date	4/29/08	4/30/08	5/1/08	-	-	-
Exhaust Gas Flow Rate	518	651	606	592	-	dscf/hr
Total VOCs	2,274	284,987	2,544	96,598	-	µg/hr
Total SVOCs	6,501	7,277	5,851	6,543	-	µg/hr
HCl	ND	ND	ND	ND	-	µg/hr
CO	11,616	23,340	23,100	19,352	9 ppm	ppm
CO	0.438	1.10	1.02	0.85	-	lbs/hr
CO ₂	8.92	9.44	13.49	10.6	-	%
O ₂	1.27	1.10	1.20	1.19	-	%
Opacity	0	0	0	0	0	% Opacity

Source: DMK Environmental Engineering CMBST test report

Table 2 Results of Air Emission Sampling for Radionuclides

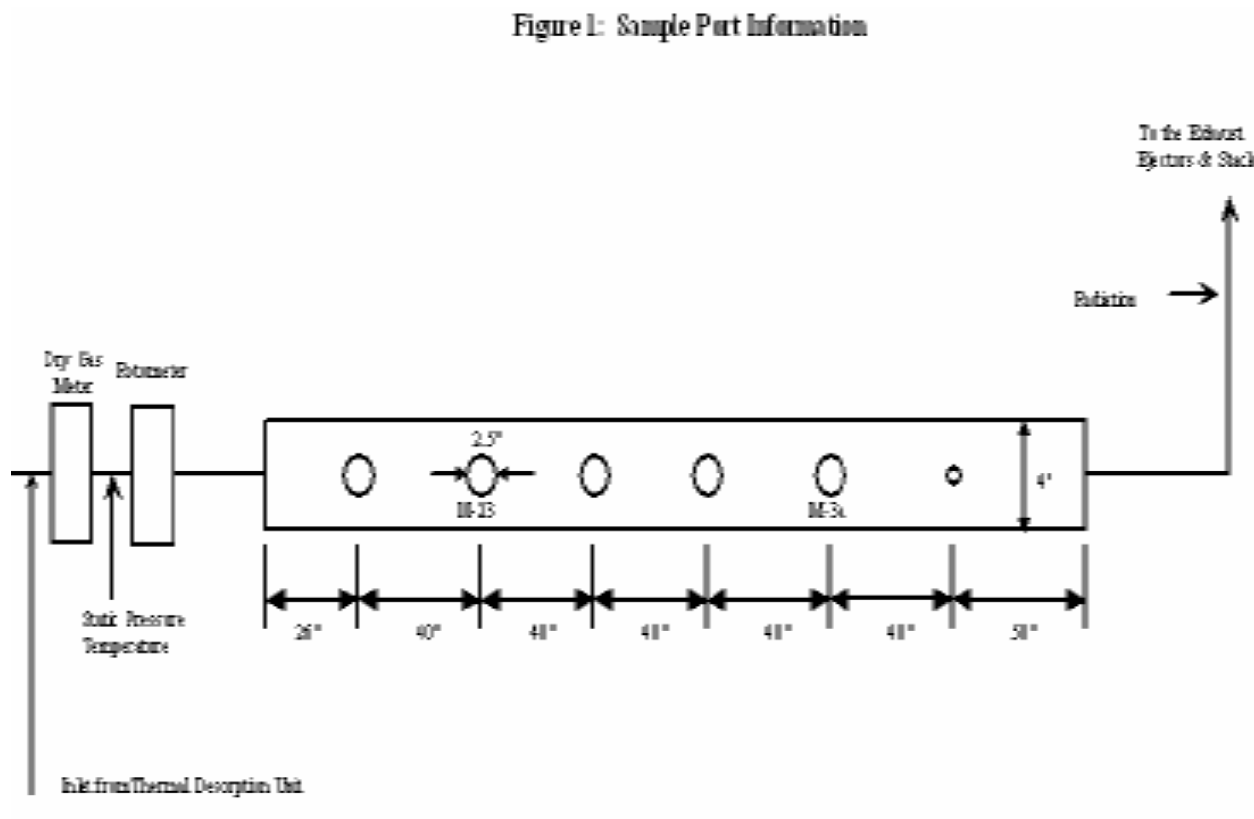
Sample ID	Start Date	Start Time	End Date	End Time	Run Hours	Standard	Volx 200 ml	Count Date	Count Time	Alphas	Betas	Ct	Aeff	Bkg	Beff	Alpha uCi/ml	Beta uCi/ml	Alpha ActLvl	Beta ctLvl			
																				Alphas	Betas	Ct
VT	4/28	13	4/29	12:	1	6	6	7704	5/2/	0.94	0.97	7	5	1	0.	0.	0.	0.	1.128291	8.381595	0.00000	0.0000

Sample ID	Start Date	Start Time	End Date	End Time	Run Hours	Standards	Volume (ml)	Count Date	Count Time	Alpha Cts	Beta Cts	Count Time	ABkg CPM	Aeff CPM	Bkg Beff CPM	Alpha uCi/ml	Beta uCi/ml	Alpha ActLvl	Beta ActLvl
D383	2008	2/28	2008	06:00	07:00	00	0000	2008	2222222	10	14	2994	02	04	047	6401526 2E-16	0411337 3E-16	000000 014	000000 021
VT D384	4/29	04/29	09:50	09:58	06:00	06:00	70560000	5/2/2008	0.948611111111	430	130	14	02	04	047	5.719583 3507736 6E-17	2.653006 7388588 6E-15	0.00000 000000 014	0.0000 000000 021
VT D385	4/29	9/28	4/29	10:38	12:07	06:00	91440000	5/2/2008	0.9555555555	77	60	14	02	04	047	9.506079 1729393 8E-17	9.777681 4350233 6E-16	0.00000 000000 014	0.0000 000000 021
VT D386	4/29	22/28	4/30	9:00	10:04	06:00	74880000	5/2/2008	0.9625	30	50	14	02	04	047	3.316681 4696794 E-17	8.416079 2293114 8E-16	0.00000 000000 014	0.0000 000000 021
VT D387	4/30	9/28	4/30	9:02	10:09	06:00	85680000	5/12/2008	0.89375	68	50	14	35	78	46	8.239811 8273456 4E-17	8.705540 3219347 4E-16	0.00000 000000 014	0.0000 000000 021
VT D388	4/30	21/28	5/1/2008	10:54	11:08	06:00	99360000	5/12/2008	0.901388888888	48	50	14	35	78	46	4.016064 5547900 8E-17	7.506951 4370306 8E-16	0.00000 000000 014	0.0000 000000 021
VT D389	5/1/2008	10/28	5/1/2008	11:20	12:04	06:00	89280000	5/12/2008	0.908333333333	210	30	14	35	78	46	3.369308 7493164 4E-16	3.541212 2569346 3E-16	0.00000 000000 014	0.0000 000000 021

Source: EnergySolutions Health Physics Department

Figure 1 Sample Port Information

Figure 1: Sample Port Information



Source: EnergySolutions state-issued Part B Permit

Table 3 Description of Air Sampling and Analytical Procedures

Parameter	Sampling Method	Analytical Method	Analytical Lab or Company
Sample Port Location	EPA 1a	NA	DMK
Stack Gas Velocity	EPA 2d	Rotameter	DMK
O ₂ & CO ₂	EPA 3a	CEMs	CCI Env
Moisture Content	EPA 5	Gravimetric	DMK/CCI Env
Visible Emissions	EPA 9	Visual	DMK
CO	EPA 10	CEMs	CCI
VOCs	EPA 0030	GC/MS	DMK/CCI Env/Test America
SVOCs	EPA 0010	GC/MS	DMK/CCI Env/Test America
HCl	EPA 26	Ion chromatography	DMK/CCI Env/Test

			America
Radionuclides	Filtered air thru LoVol sampler from off-gas line	α/β & Isotopic	In-house & GEL
I Radionuclides H ₃	Grab from off-gas line	Isotopic	GEL

Source: DMK Environmental Engineering CMBST test report

Table 4 Exhaust Gas Flow Rate

	Date	ACFM	Temp (°F)	Pressure (in. Hg)	Static Pressure (in. H ₂ O)	Moisture (%)	DSCF M	DSCF/hr
CMBST-1	4/29/08	10.6	80.45	25.38	-0.56	1.50	8.64	518
CMBST-2	4/30/08	12.96	64.39	25.32	-1.13	1.45	10.85	651
CMBST-3	5/1/08	12.08	71.89	25.56	-1.0	1.1	10.1	606
Average		11.88	72.74	25.42	-0.9	1.35	9.86	592

Source: DMK Environmental Engineering CMBST test report

Table 5 CO lbs/hr

	Mol Wt (lb/lb-mol)	PPM	Flow Rate (dscf/m)	Emission Rates	
				(lbs/hr)	(mg/m ³)
CMBST-1	28.01	11,616	8.64	0.438	13,534
CMBST-2	28.01	23,340	10.85	1.10	27,194
CMBST-3	28.01	23,100	10.1	1.02	26,915
Average	28.01	19,352	9.86	0.85	22,548

Source: DMK Environmental Engineering CMBST test report

Table 6 Radiological Counting Analysis

	Alpha ($\mu\text{Ci/mL}$)	Beta ($\mu\text{Ci/mL}$)
CMBST-1	9.29×10^{-17}	5.89×10^{-16}
CMBST-2	8.18×10^{-17}	5.28×10^{-16}
CMBST-3	3.24×10^{-16}	2.11×10^{-16}

CONCLUSION

At the time of writing, the data are still under regulatory review but preliminary reviews indicate that the processed material meets LDR standards and the emissions meet permit conditions.

REFERENCES

DMK Environmental Engineering Inc. *EnergySolutions, LLC Mixed Waste Thermal Desorption Unit, CMBST, April 29-May 1, 2008,*

EnergySolutions LLC Mixed Waste Storage, Treatment and Disposal Permit, 2003, Utah Solid and Hazardous Waste Control Board.

EnergySolutions LLC VTD Post-CMBST Report, July 15, 2008.