CONF-950877--25

Abstract # MWS045



# TREATMENT OF Y-12 STORM SEWER SEDIMENTS AND DARA SOILS BY THERMAL DESORPTION

By:
M. I. Morris
Oak Ridge National Laboratory
Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee
Tel (615) 574-0559

* S. E. Shealy
IT Corporation
304 Directors Drive
Knoxville, Tennessee 37923
Tel (615) 694-7447
Fax (615) 694-9573



Submitted to:
**ASME Third Biennial Mixed Waste Symposium**
August 7-11, Baltimore, Maryland

## Abstract

The 1992 Oak Ridge Reservation Federal Facilities Compliance Agreement (FFCA) listed a number of mixed wastes, subject to land disposal restrictions (LDR), for which no treatment method had been identified, and required DOE to develop strategies for treatment and ultimate disposal of those wastes. This paper presents the results of a program to demonstrate that thermal desorption can remove both organics and mercury from two mixed wastes from the DOE Y-12 facility in Oak Ridge, Tennessee. The first waste, the Y-12 Storm Sewer Sediments (SSSs) was a sediment generated from upgrades to the plant storm sewer system. This material contained over 4 percent mercury, 2 percent uranium and 350 mg/kg polychlorinated biphenyls (PCBs). Leachable mercury exceeded toxicity characteristic leaching procedure (TCLP) and LDR criteria. The second waste, the Disposal Area Remedial Action (DARA) Soils, are contaminated with uranium, mercury and PCBs. This treatability study included bench-scale testing of a thermal desorption process.

Results of the testing showed that, for the SSSs, total mercury could be reduced to 120 mg/kg by treatment at 600°C, which is at the high end of the temperature range for typical thermal desorption systems. Leachable TCLP mercury was less than 50 $\mu$g/L and PCBs were below 2 mg/kg. Treatment of the DARA Soils at 450°C for 10 minutes resulted in residual PCBs of 0.6 to 3.0 mg/kg. This is too high (goal $<$2mg/kg) and higher treatment temperatures are needed. The testing also provided information on the characteristics and quantities of residuals from the thermal desorption process.

Abstract # MWS045

## ACRONYMS

| | |
|---|---|
| $\mu g/L$ | microgram(s) per liter |
| CCW | constituted concentration in treated waste |
| CCWE | constituted concentration in treated waste TCLP extract |
| DARA | Disposal Area Remedial Action |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| FFCA | Federal Facility Compliance Agreement |
| HEPA | high-efficiency particulate absolute |
| LDR | land disposal restrictions |
| mg/L | milligrams per liter |
| mg/kg | milligram(s) per kilogram |
| NA | nct analyzed |
| ND | not detected |
| O & G | oil and grease |
| PCB | polychlorinated biphenyls |
| R&D | Research and Development |
| RCRA | Resource Conservation and Recovery Act |
| RTA | Rotary Thermal Apparatus |
| SSSs | Storm Sewer Sediments |
| TCLP | toxicity characteristic leaching procedure |
| TOC | total organic carbon |
| TOX | total organic halides |
| TSCA | Toxic Substances Control Act |
| VOC | volatile organic compound |

## 1.0 INTRODUCTION

**BACKGROUND**

The 1992 Federal Facility Compliance Agreement (FFCA)[1] for the Oak Ridge Reservation listed a number of wastes that were subject to Land Disposal Restrictions (LDR), and for which no treatment method had been identified. The FFCA required that DOE develop strategies for treatment and ultimate disposal of these wastes. This report presents the results of a treatability study designed to demonstrate that thermal desorption can remove both organics and mercury from two mixed wastes from the Department of Energy Y-12 facility in Oak Ridge, Tennessee. The first waste, the Y-12 Storm Sewer Sediments (SSSs) was a sediment generated from upgrades to the plant storm sewer system. This material contained over 4 percent mercury, 2 percent uranium and 350 mg/kg polychlorinated biphenyls (PCBs). Leachable mercury exceeded TCLP and LDR criteria[2]. The second waste, the Disposal Area Remedial Action (DARA) Soils, are contaminated with uranium, mercury and PCBs. These soils were removed from an oil pond that was located in the Bear Creek Burial Grounds at the Y-12 Plant. The DARA soils are currently in RCRA storage at the Y-12 facility, while the SSSs are in B-25 boxes.

The treatability study included lab and bench-scale tests designed to demonstrate that wastes treated by thermal desorption would meet disposal criteria for PCBs and mercury[3]. Disposal criteria were initially set by TCLP criteria for mercury and by TSCA PCB limits. The thermal desorption technology used in this study was developed for removal of organics from contaminated soils and has been tested on a limited number of mercury contaminated wastes. This paper outlines the experimental program, test apparatus, experimental observations and discusses the results of the study.

**TECHNOLOGY DESCRIPTION**

This thermal desorption technology is based on indirect heating of soil or wastes using a rotary calciner. The soil is heated to temperatures between 350 and 650 degrees Celsius (°C) and held at that temperature for 5 to 20 minutes. These conditions are typically sufficient to desorb the organics and mercury from the soil. In a full-scale thermal desorber, prepared soil is continuously charged into the calciner or kiln through the feed system (i.e., an air lock isolation valve and feed chute or a screw feeder). The material is heated and desorbed as it is conveyed through the inclined rotating unlined metal desorber tube. The tube is indirectly heated by firing natural gas into a stationary insulated chamber (furnace) surrounding the rotating tube. The feed material is heated to 350° to 600°C and held at that temperature long enough to desorb water, mercury and organic contaminants. The treated material is discharged by gravity into the treated material handling system for cooling and remoisturization.

A counter-current purge (sweep) gas is introduced to the desorber through the solids discharge hood. The sweep gas can be steam, air, nitrogen (or inert gas), recycled desorber off-gas, or combustion gas (principally nitrogen, water vapor and carbon dioxide) from the natural gas burners firing the furnace. The desorber is operated under a slight negative pressure produced by an induced draft fan located downstream of the gas cleaning (air pollution control) system. The gas leaving the desorber consists of the purge gas, water, mercury, and organic vapors, entrained soil particles, and any radionuclides associated with these particles. The desorber off-gas is treated in a gas cleaning system that can include condensers, wet scrubbers, and carbon absorbers. The gas cleaning system configuration depends primarily on the soil contaminants and the properties of the soil fines.

**TREATABILITY STUDY APPARATUS**

This treatability study was conducted in two stages. The screening stage used laboratory-scale, range finding tests to identify effective treatment conditions, which were then used in the bench-scale confirmation tests. This program utilized three types of laboratory and bench-scale apparatus: tray tests, tube furnace tests, and Rotary Thermal Apparatus (RTA) tests. Tube furnace tests and static tray tests are simple lab-scale procedures that are used to rapidly screen the conditions (time and temperature) required to meet the treatment criteria for the soil or waste. These tests provide a qualitative indication of the effects of thermal treatment on the waste, and data on total weight loss. These tests are typically performed by heating approximately 50 grams of soil in a quartz tube or alloy tray in a small electric furnace.

The RTA is a larger bench-scale device that is used to treat up to a kilogram of soil in an electrically heated rotary tube. This device simulates the heat and mass transfer in a full scale rotary kiln or calciner. The RTA is a batch device and can be purged with a variety of gases, such as nitrogen, oxygen-deficient or oxygen-rich air, or steam to simulate the atmosphere of various thermal treatment processes. The RTA is used to confirm the results of the tray/tube tests, generate information on the gases desorbed from the waste during processing, provide small quantities of process residuals, and to generate larger quantities of treated waste for chemical and physical analyses.

**TREATABILITY STUDY OBJECTIVES**

The primary purpose of the treatability study was to demonstrate that thermal desorption could meet the performance requirements for removal/reduction of PCBs and mercury from the DARA Soils and SSSs. These performance requirements or treatment criteria for these two wastes are shown in Table 1-1. The 12 ppm treatment standard for total mercury was based on disposal in an on-site landfill. Disposal at an off-site permitted facility requires that the material meet the LDR total mercury limit of 260 ppm, or that it be further treated by retorting and also meet TCLP[2].

This study was also designed to generate limited data on the fate of the mercury, PCBs and uranium during thermal treatment and on other contaminants in the residuals recovered from the off-gas treatment system.

# 2.0 EXPERIMENTAL DESIGN AND PROCEDURES

## TREATABILITY STUDY SUMMARY

This treatability study was conducted in accordance with the Treatability Study Work Plan[4] and Quality Assurance Project Plan[5] that were approved in December, 1994, by Martin Marietta Energy Systems. This test program was conducted in two stages. The screening stage used laboratory-scale, range finding tests in the tube and tray apparatus, to identify effective treatment conditions which were then used in the bench-scale confirmation tests in the RTA. The study was conducted at a commercial treatability laboratory under an existing TSCA research and development (R&D) permit and facility radioactive materials license.

The Y-12 Storm Sewer Sediments (SSSs) were received on May 18, 1994 and logged into the laboratory sample tracking system. They were then screened to remove oversize material and mixed to ensure that the sample was homogenized. Oversize material is not included in the test soil. Homogeneity was confirmed by analyzing multiple samples for mercury. Initial mercury was greater than 4 percent and PCBs were 350 mg/kg. Tube furnace tests were conducted at 450°C and 550°C with different treatment times and using air, nitrogen and steam as purge gases. The treated soil from these tests had 50 to 100 mg/kg residual mercury and PCB concentrations below 2 mg/kg. TCLP mercury was below the treatment criteria. Purge gas did not seem to affect residual mercury. A series of tray tests were conducted under more aggressive treatment conditions but still did not produce treated SSSs with less than 50 mg/kg mercury. RTA tests were conducted at 600°C with an air purge and 350°C with a steam purge. The treated soil from the two 600°C runs met criteria for PCBs and TCLP mercury with total mercury of 82 and 141 ppm.

The DARA soils were received on August 4, 1994 and logged into the sample tracking system. They were screened to remove oversize material and mixed to ensure that the sample was homogenized. Homogeneity was confirmed by analyzing multiple samples for mercury. Initial mercury was 0.7 mg/kg and PCBs were 75 mg/kg. Tray furnace tests were conducted at temperatures between 350°C and 550°C, with treatment times of 0 to 20 minutes. The treated soil from these tests had less than 0.04 to 1 mg/kg residual PCBs. Treatment at temperatures at or above 425°C resulted in less than 0.5 mg/kg PCBs. RTA tests were conducted at 400°C and 450°C with an air purge. Results were surprising with residual PCBs in all treated soils of 0.6 to 3.0 mg/kg. The duplicate RTA runs at 450°C/10 minutes had 0.6 and 3.0 mg/kg PCBs. Higher treatment temperatures are recommended. The treated soil from all four RTA runs met criteria for TCLP and total mercury.

The following sections will provide more detailed descriptions of the experimental apparatus, the test conditions, the sample descriptions and the analyses performed.

## TEST APPARATUS

### Tube Test Apparatus

The tube furnace is a 1-inch-diameter by 16-inch-long static quartz tube positioned in a Lindberg Model 851 furnace. The inlet and outlet portions are designed so that the gas atmosphere in the tube can be adjusted and then collected for characterization. For these tests, a cold finger condensing system was used.

The temperature of the furnace is controlled by a feedback loop to an external miniature Omega proportional controller from a thermocouple positioned in the sample inside the tube. The feedback to this controller can also be taken from another location in the system such as the exterior glass wall inside the furnace. This temperature, as well as the temperature of the sample inside the tube, the temperature of the gas coming into the tube, and the temperature of the heating tape on the glass inlet preceding the furnace portion, are recorded using a Yokogawa Model 3800 multi-point recorder equipped with an RS232 port so that data can also be logged directly by a computer.

Air, nitrogen and steam were tested as purge gases. Steam is generated in an electrically heated half-inch stainless steel tube. The flow is controlled with the pump that feeds the water to the tubing. The steam enters the quartz tube in the furnace through the heated annular space of the inlet adapter. The gases exiting the tube are condensed on a pair of cold fingers in ice baths in series, pass through a small carbon adsorber, and are vented into the hood. The entire system is positioned inside a fume hood. The exhaust from the hood is filtered by high-efficiency particulate absolute (HEPA) filters.

The main steps of this procedure are as follows:

- Place a loose plug of glass wool in the exit end of the quartz furnace tube, transfer a representative aliquot 35 to 50 grams of prepared soil from to the tube using a stainless steel spatula. Place another plug of glass wool in the inlet of the tube.

- Place the soil packed tube in the furnace (at ambient temperature) and connect the inlet and exit glassware. Turn on the purge gas flow.

- Set the oven temperature controller set-point to target test temperature and start the timer.

- Monitor and record the temperatures and time periodically throughout the test period and record any pertinent observations.

- When the prescribed residence time at the target temperature is reached, shut off the oven heater, open the oven and allow the furnace and tube to cool. The inlet and outlet glassware are then disconnected and so that the soil can be removed and submitted for analysis. The tube should be decontaminated carefully between runs.

**Tray Test Apparatus**

The tray test apparatus and procedures are essentially identical to that described in the EPA's guidance for conducting treatability studies.[8] The experimental apparatus for this phase of the test program consisted of a Lindberg Model 51848 muffle furnace with an electronic temperature controller and a 1,600-watt heater and a similar Lindberg Model 51748 oven with an analog controller. The ovens had double shell construction with interior surfaces made of Moldatherm®, a molded aluminum-silicate insulation material. The ovens were capable of operating at temperatures up to 1100°C and had a relatively fast heatup rate due to a low mass. The interior space was approximately 3.9 inches wide by 4.3 inches high by 8.3 inches deep. A loose block (0.5-inch-thick) of Moldatherm® placed on the bottom of the oven provided additional separation between the tray and the hot interior surface of the oven.

A specially designed tray was used to contain the waste sample within the oven. The tray, which weighed approximately 450 grams, is 3.5 inches wide by 1.3 inches high by 7.6 inches long and was constructed of Incoloy to resist oxidation during high temperature tests.

The standard operating procedure (SOP) for the tray tests are as follows:

- Transfer a representative aliquot of prepared soil from the jar to the tray using a stainless steel spatula.

- Weigh the soil and tray and adjust the soil quantity to achieve a uniform layer in the bottom of the tray, usually a 2 to 3 mm depth for a 30 to 100 g aliquot of soil.

- Turn on the purge gas flow and place the tray with the soil in the oven at ambient temperature and close the oven door.

- Set the oven temperature controller set-point to target test temperature and start the timer.

- Monitor and record the temperatures and time periodically throughout the test period and record any pertinent observations.

- When the prescribed residence time at the target temperature is reached, shut off the oven heater, open the oven door and remove the tray. Allow the tray to cool and submit the treated soil for analysis. The trays should be decontaminated carefully between runs.

**RTA Test Apparatus**
The RTA is a rotating tube, thermal unit, used to evaluate the effect of time, temperature, and atmosphere for the thermal treatment of solids and sludges. Treated residues from the tests will provide adequate sample for analysis.

This custom designed and fabricated unit is designed to operate in the batch mode. The rotating tube portion of the system is 5 inches in diameter by 12 inches long and is fabricated from Incoloy™ to resist oxidation during high temperature tests. The cylinder rotates at 5 revolutions per minute and is externally heated with a custom made 7000 watt Lindberg furnace. The chain-driven tube is suspended on both ends by brass rollers and sealed by graphite packing rings at the inlet and outlet distribution boxes. The heat-up rate and operating temperature of the furnace are controlled with a Lindberg 59554-B temperature controller. Temperatures of the solids in the tube and the gases in the rotating cylinder are measured with two type-K thermocouples calibrated against a National Bureau of Standards (NBS) traceable standard. These temperatures and the temperature of the oven and other off-gas system temperatures are recorded on a Yokogawa Model 3800 multi-point recorder equipped with an RS232 port for computer data logging.

The off-gases (purge gas and desorbed constituents) from the cylinder exit through a 3-foot-long quartz tube into the off-gas treatment systems.

Pressure in the RTA cylinder is maintained at a slight vacuum of at least minus 0.15 inches of water to ensure no external leakage from the system. For this project, the RTA was purged by air and steam which will be produced by a small electric steam generator. Steam flow was controlled by metering the water into the steam generator with a tubing pump. A rotameter was used to measure the non-condensible fraction of the off-gas exiting the gas treatment system through the vacuum pump.

Figure 2-1 illustrates the RTA and the off-gas system. The main steps of the procedure are described below:

- The soil or waste for the test is mixed for homogeneity, debris is removed by hand and 500 to 1000 g of material is charged to the treatment cylinder which is then bolted into the RTA.

- The off-gas sampling systems are connected to the RTA and purge gas, a mixture of nitrogen and oxygen, is set to the required rate of 1-3 liters per minute. The cylinder rotation is set at 5 rpm.

- The furnace is preheated to 200°C above the desired treatment temperature. It is then raised and clamped around the treatment cylinder.

- The temperature of the soil is monitored and the set point of the furnace is adjusted. The furnace is carefully opened to avoid overshooting the desired soil temperature.

- After the soil treatment time is reached, the furnace is turned off and removed from the treatment cylinder which is then cooled by a fan.

- Purge gas is shut down and the unit disassembled when soil reaches ambient conditions.

## EXPERIMENTAL TEST PROGRAM

### Screening Test Matrices

For the SSSs, the initial range-finding screening tasks were conducted in the tube furnace apparatus. The final thermal tests to verify the screening results were conducted in the RTA. For the tube furnace tests, treatment temperatures of 450°C and 550°C for 10 to 20 minutes at treatment temperature were selected based on prior experience with wastes containing PCBs and mercury. The effect of air, nitrogen and steam as purge gas was also tested.

The tube furnace experiments on the SSSs, revealed that mercury was not being reduced to the target level of 12 mg/kg. Therefore, additional tray tests were conducted at more aggressive time/temperature conditions (i.e., higher temperature and longer time at temperature). These included 4 tests at 550°C with treatment times of 20, 40, 60 and 90 minutes at temperature and 4 tests at 550°C, 600°C, 650°C and 700°C at a treatment time of 10 minutes at temperature. These time temperature conditions include the upper end of the range of treatment conditions that can be achieved in typical indirectly-fired, rotating tube systems. Treated soil from these tests still contained 50 to 100 mg/kg mercury which for this waste appears to be the lowest level obtainable with this technology.

The results of the screening tests on the SSSs showed that purge gas had little if any effect on mercury removal and that there was no significant difference between the tube and tray tests. Based on these two findings, the screening tests, on the DARA soils were done in the tray test apparatus. The primary contaminant of concern in the DARA soil was the 75 mg/kg of PCBs. The tests conditions ranged from treatment at 350°C for 5 minutes to 550°C for 10 minutes.

### RTA Test Matrices

On the SSSs, four RTA tests were run at two sets of conditions (duplicate tests). The first two RTA tests were run at 600°C with a treatment time of 10 minutes and an air purge at 1800 mL/minute. These conditions represent the upper end of the temperature range that can be achieved by typical thermal desorption equipment. The second set of RTA tests were conducted at 350°C with a treatment time of 10 minutes and a steam purge of 3000 mL/minute. These conditions were selected because the tube test run 6A at 450°C and 10 minutes (steam purge, least aggressive conditions tested) gave the lowest final mercury of all the tube tests. There was some concern that the more aggressive treatment conditions were converting the mercury to a non-volatile form. These two RTA runs were therefore designed to determine the mercury removal at the lower range of the treatment conditions.

The tray tests, on the DARA soils indicated that treatment at temperatures of 425°C and higher resulted in residual PCBs below 0.5 mg/kg. Accordingly the RTA tests on the DARA soils were run at 400°C with no time at treatment temperature (i.e., cool down was started when soil hit 400°C) and at 450°C for 10 minutes. Duplicate runs on both sets of conditions were conducted.

These experiments also provided data about the nature of the residue that will be generated in the RTA off-gas treatment system. This data can be used to evaluate pilot-plant off-gas treatment system configurations prior to pilot-plant testing.

## 3.0 EXPERIMENTAL RESULTS

### WASTE HOMOGENIZATION AND CHARACTERIZATION

#### Storm Sewer Sediments

SSSs sample was received in a 5-gallon metal can at the laboratory on May 18, 1994. The sample was logged into the laboratory sample tracking system as sample GG5988. The metal can weighed at 28.0 kg (61.74 lb) and was opened for inspection on May 19, 1994. The top soil appeared very dry, dusty, and contained small stones that were up to ½" size. In addition, the soil contained pieces of wood, twigs, and metal shavings. The material was screened through 0.25-inch hardware cloth. There were spots of white material throughout the sample, but no observable beads of elemental mercury. The oversized material, screened from the sample, weighed 3.882 kg (8.56 lb). For homogenization purpose, samples were turned on a tray that was placed inside a plastic bag to minimize dusting. Aliquots were taken for mercury analysis in 5-mL vials.

The material was mixed and homogeneity was confirmed by mercury analysis of 10 samples. Average mercury content in the storm sewer sediment was 42,458 mg/kg. Total activity of the sample was 38,000 pico-curies per gram, with total uranium of 1.9 percent by ICP method. Initial PCB concentration was 350 mg/kg. Analyses of the untreated soil are shown on Table 3-5.

After the homogeneity analysis was complete and relative standard deviation (RSD) was determined to be less than 20 percent, the sample was transferred back to the 5-gallon metal can. The oversize screenings were placed in a plastic bag, and placed at the bottom of the metal can. The sample itself was placed in the metal can using a large scoop with the transfer taking place inside the large garbage bag and inside the fume hood to minimize dusting.

**DARA Soil**

DARA Soil sample was received in a 5-gallon pail (labeled HP-3) on August 4, 1994. The sample weighed 17.2 kg (38 lb). The sample was logged into the laboratory sample tracking system as sample GG6102. A strong odor of decaying soil was noticed upon breaking the sample lid seal. The material appeared as a very moist clay with stones ranging in size up to 1 inch.

The material was screened through 0.25-inch hardware cloth. Approximately half of the material passed on the first round, and the remainder of the material consisted of lumps of wet clay soil and clay covered stones. The material was then allowed to air-dry for 36 hours. Prior to air-drying an aliquot of the "as received" material was removed for radiological screening and initial moisture analysis. The dried material was screened and crushed by hand and homogenized on a large plastic sheet inside the fume hood. After drying all of the DARA soil passed the screen and no oversize material was collected. The homogenized material was sampled for moisture analysis on August 8, 1994, and for mercury analysis. The "as received" soil moisture was 19.6 percent, while the moisture of the air dried homogenized material was 12.5 percent. Initial PCB concentration was 75 mg/kg. Other analyses of the untreated soil are shown on Table 3-6.

## TRAY AND TUBE TESTS

### Storm Sewer Sediments

**Tube Tests**

During the tube furnace tests elemental mercury condensed on the walls of the tubing and glassware used in the condensation system. Where possible this mercury was recovered and weighed. The nitrogen purged runs produced a completely charred residue an slight oily film above the condensate. The steam purge produced a yellow or grayish oily layer.

The steam purged soils appeared to have less overall charring than other tests. The air purge produced a lighter colored soil in the regions where sufficient air reached the soil. For the first three tests, only about ¼" of the leading edge of the sample was a light brown color.

The results of the initial tube furnace tests are shown on Table 3-2 and were not as expected. Although leachable mercury, as measured by TCLP extraction, was below the treatment criteria for all conditions, the treated soil did not meet the total mercury criteria of 12 mg/kg. Treated soils at all conditions had residual mercury levels ranging between

50 and 100 mg/kg. For all of the tube tests, there was no clear correlation between treatment conditions and residual mercury. Residual mercury did not consistently go down with more aggressive treatment conditions.

The PCB analysis of the residue from the first eleven tests were all below 2 mg/kg total PCB except the first air test at 450°C for 10-minutes which had 7.3 mg/kg residual PCB. The samples had a large interference peak in the chromatogram, which in most cases was eliminated by a cleanup procedure that is designed to eliminate sulfur interferences. The starting PCB concentration was 274 mg/kg which was mostly Aroclor 1260.

In addition to the initial series of 11 tube tests, four additional tests were run. A 550°C/20 minute test, with an increased air purge rate, gave a treated soil with 90 mg/kg mercury. A 700°C/10 minute test resulted in a treated soil with 54 mg/kg of mercury in the first half of the bed and 61 mg/kg in the back end. In a 550°C/30 minute test, with a steam purge, the soil was divided into thirds which all had similar mercury concentrations of 62 to 90 mg/kg. These two tests, with the analysis of the split soil beds were conducted to determine if there was a mercury 'profile' in the treated soil bed. If mercury in the back end of the bed was higher than in the front of the soil bed, inadequate purge rate would have been expected. The main conclusion from the tube tests was that although 99.8% of the mercury was removed, the SSSs contained 100 mg/kg of a very non-volatile mercury species.

**Tray Tests**

When the initial tube furnace tests showed that mercury in the treated soil was above the 12 mg/kg criteria a series of 9 tray tests were conducted. The results of the tray tests are shown on Table 3-3. In the first four of these tests, higher temperatures were tested. The tray test conditions were 550°C, 600°C, 650°C and 700°C with a 10 minute treatment time for all tests. The 700°C temperature represents the high end of the economical operating range of typical indirectly fired thermal desorption systems. Mercury in the treated SSSs did seem to decrease with increased temperature but only from 113 to 72 mg/kg. In the second set of tray tests, treatment temperature was 550°C and treatment times were 20, 40, 60 and 90 minutes.

Increased treatment time did not seem to affect residual mercury. The results of the tube and tray tests, demonstrated that 50 to 100 mg/kg residual mercury was the lower limit for treatment in typical indirectly fired rotating tube type thermal desorption systems.

**DARA Soils**

Tray tests were conducted at temperatures of 350°C, 425°C, 500°C and 550°C with treatment times of 0, 5, 10 and 20 minutes at temperature. All treated soils were somewhat charred which typically indicates a higher level of organic material (not necessarily contaminants). Results of these tests are shown in Table 3-4. The residual

PCBs in the treated soil from these tests ranged from less than the detection limit of 0.04 mg/kg to 1 mg/kg. Treatment at temperatures at or above 425°C resulted in less than 0.5 mg/kg PCBs at all treatment times.

## RTA TESTS

### RTA Tests on Storm Sewer Sediments

All RTA results for the SSSs are shown on Table 3-5. Four RTA tests were run at two sets of conditions (duplicate tests). The first two RTA tests were run at 600°C with a treatment time of 10 minutes and an air purge at 1800 mL/minute. These conditions represent the upper end of the temperature range that can be achieved by typical thermal desorption equipment. The treated storm sewer sediments from these two runs contained 82 and 141 mg/kg of total mercury. Leachable mercury for both runs was below the detection limit of 0.002 mg/L. Both PCBs were also below 2 mg/kg. Much of the mercury that was desorbed from the soil was collected as elemental mercury in the off-gas condenser system as grey solids. The scrubber water and condensate in the impinger also had 371 and 94 mg/L of mercury, 2.1 and 0.3 mg/L of PCBs and 390 pico curie per gram of uranium activity. The variability of the mercury and PCB values probably indicate that the contaminants are adsorbed on fine solids in the condensate.

The second set of RTA tests were conducted at 350°C with a treatment time of 10 minutes and a steam purge of 3000 mL/minute. These conditions were selected because the tube test run 6A at 450°C and 10 minutes (steam purge, least aggressive conditions tested) gave the lowest final mercury of all the tube tests. These RTA runs were designed to determine the mercury removal at the lower range of the treatment conditions. (There was some concern that the more aggressive treatment conditions were converting the mercury to a non-volatile form.) The results of these runs showed that final mercury was very high, 3700 and 4100 mg/kg. TCLP mercury for the treated soil was still below the detection limit of 0.002 mg/L. PCBs were also just above the treatment criteria of 2 mg/kg at 2.5 and 3.1 mg/kg. The condensate analysis for PCBs and mercury was similar to the previous runs. Analysis of the condensate from the two 350°C runs also showed 108 mg/L of volatile organic halides and 696 mg/L of oil and grease. This indicates the presence of organics other than PCBs. This is confirmed by the VOC analysis which showed 29 and 5 mg/L of acetone and 1-butanone as well as 10 mg/L of unidentified volatiles. The organics in the condensate probably did not come from the untreated soil (it has been dried and mixed and VOCs should have been lost) but are more likely from pyrolysis of other soil organics. The treated soil also showed 0.4 mg/kg acetone and 0.027 and 0.120 mg/kg of benzene (repeat analyses).

**RTA Tests on DARA Soils**

RTA tests were conducted at 400°C and 450°C with an air purge. Treatment time was 5 minutes at 400°C and 10 minutes at 450°C. Results, shown in Table 3-6, were surprising with residual PCBs in all treated soils at 450°C/10 minutes had 0.6 and 3.0 mg/kg PCBs. The duplicate runs at 400°C/5 minutes had 2.3 and 2.9 mg/kg PCBs. Previous tests[6,7] had indicated that 450°C/10 minutes was adequate for PCB removal. The treated soil from all four RTA runs met criteria for TCLP and total mercury. The treated soils were re-analyzed for PCBs by the treatability lab analytical group and the presence of residual PCBs was confirmed on all samples.

The condensate (scrubber solution) from the RTA runs contained 1 to 3 grams of oily sludge. This sludge was removed from the condensate and analyzed separately for PCBs. The sludge contained 1.6 to 15.6% PCBs. The condensate also contained low levels of PCBs after filtration. The condensate also contained 580 mg/L of oil and grease, again indicating the presence of other organics in the RTA off-gas. The VOC analysis of the condensate showed 110 mg/L of acetone, 43 mg/L of 2-butanone and 2.4 mg/l of hexanone. The treated soil had 0.9 mg/kg of acetone and 0.1 of 2-butanone. These are probably formed by pyrolysis of soil organics. Mercury levels in the condensate were 0.01 and 0.03 mg/L which is in the range of the TCLP limit of 0.6 to 3.0 mg/kg.

## 4.0 RESULTS AND CONCLUSIONS

**Y-12 STORM SEWER SEDIMENTS**

Y-12 Storm Sewer sediments treated by thermal desorption at 450° to 600°C should meet criteria for disposal in an off-site mixed waste landfill. PCBs and leachable mercury can be reduced to well below the treatment criteria of 2 mg/kg for PCBs and the TCLP limit of 0.2 mg/L leachable mercury. Total mercury can also be reduced to below the LDR criteria of 260 mg/kg. The most significant finding of this study was that although most of the mercury in the Y-12 storm sewer sediments was readily removable by thermal desorption, there is 50 to 120 mg/kg (out of the starting 47,000 mg/kg) that is not volatile at conditions achievable by thermal desorption systems that are typically used for remediation of soil contaminated by organics. This mercury is, however, not leachable. Based on the low TCLP mercury on the SSSs treated at 350°C the leachable mercury is very readily volatilized and is probably in the elemental form. Even the 3700/4100 mg/kg of residual mercury in this treated SSSs was not leachable. SSSs treated at 350°C does not meet the LDR criteria of 260 mg/kg total mercury and would require retorting before disposal. Treatment at higher temperatures will eliminate this additional cost. The tube and RTA tests indicate that 450°C is probably a minimum temperature for meeting the criteria of 260 mg/kg total mercury, 0.2 mg/kg leachable mercury and less than 2 mg/kg PCBs. The screening phase of this study, conducted in the tube furnace apparatus, also showed that using different purge gases (nitrogen, air and steam) had no effect on residual mercury concentrations.

Analysis of the condensate resulting from treatment of this waste indicates that it will contain fine solids containing uranium, PCBs and elemental mercury, dissolved mercury and organics other than PCBs. The organics include VOCs and compounds that were measured as TOX and oil and grease. These organics probably did not come from the untreated soil (it has been dried and mixed and VOCs should have been lost) but are more likely from pyrolysis of other soil organics (both contaminants and natural humic material).

If the full-scale thermal desorption system uses a wet scrubber as part of the emissions control system, the condensate can be recycled within the scrubber system. Discharge of this condensate will require substantial treatment and will produce mixed waste residuals requiring disposal or further treatment to reduce mercury leachability. Based on the amount of mercury solids collected from the RTA off-gas system during the tests, 30 to 70% of the mercury in the untreated soil will be recovered in the thermal desorption system as elemental mercury adsorbed on soil fines. Some, if not most, of the off-gas treatment system residuals will also be a TSCA waste. The volume of these residuals will be much lower than the volume of the SSSs. Chemical dechlorination may be needed to destroy PCBs in the scrubber residuals to allow disposal in existing RCRA mixed waste facilities. Stabilization or amalgamation will be required to reduce TCLP mercury to acceptable limits.

**DARA SOILS**

This study did not demonstrate that treatment of DARA soils by thermal desorption at the tested conditions can meet disposal criteria for PCBs. Experience with other wastes indicates that higher temperatures can further lower PCB levels. Since treatment at 450°C for 10 minutes resulted in 0.6 and 3.0 mg/kg PCBs, it is reasonable to expect that more aggressive conditions (550°C/10 minutes) will bring residual PCBs below the treatment criteria.

The condensate from treatment of this waste will contain an oily sludge phase that will be high in PCBs. This sludge will require treatment in the TSCA incinerator or by chemical dehalogenation. The potential for this stream to contain mercury (the RTA runs did not generate enough for analysis) may make it a poor candidate for the TSCA incinerator. The aqueous fraction of the off-gas will contain low levels of PCBs (0.2 to 0.4 mg/L) and mercury which should be removed by treatment. Residuals from treatment of the condensate may require stabilization or amalgamation to reduce mercury leachability or PCB content. Again volume reduction will be substantial.

## References

[1]USDOE/USEPA. Oak Ridge Reservation Federal Facilities Compliance Agreement. Docket 92-02-FFR; 1992.

[2]USEPA. Land Disposal Regulations-Treatment Standards for Hazardous Waste. 40 CFR 268.40. 59 Fed. Reg. 48046; 1994.

[3]USEPA. Toxic Substances Control Act. 40 CFR 761; 1994.

[4]IT Corporation. Treatability Study Work Plan for Treatment of DARA Soils and Y-12 Storm Sewer Sediments by Thermal Desorption; 1994.

[5]IT Corporation. Quality Assurance Project Plan for Treatment of DARA Soils and Y-12 Storm Sewer Sediments by Thermal Desorption; 1994.

[6]Alperin E. S.; Fox, R. D. Thermal Treatment for the Removal of PCBs and Other Organics from Soil. Environmental Progress (Vol. 10, No. 1); 1991.

[7]Groen, A.; Shealy, S. E. Fate of Contaminants and Other Organics During Treatment of Wastes by Thermal Desorption. Proceedings of AWMA Annual Meeting, Cincinnati, Ohio, June 19-24, 1994.

[8]USEPA. Guide for Conducting Treatability Studies Under CERCLA; Thermal Desorption. EPA/540/R-92/07413; 1992.

**Table 1-1**

**Performance Requirements**

| DARA Soils Treatment Standard | | |
|---|---|---|
| **Contaminant** | **Constituent Concentration in Treated Waste (CCW)** | **Constituent Concentration in Treated Waste TCLP Extract (CCWE)** |
| Mercury | 12 mg/kg[a] | 0.02 mg/L[b] |
| Total PCBs | 2 mg/kg | -- |
| Aroclor 1242 | 0.92 mg/kg[c] | -- |
| Aroclor 1254, 1260 | 1.8 mg/kg | -- |

| Storm Sewer Sediments Treatment Standard | | |
|---|---|---|
| **Contaminant** | **Constituent Concentration in Treated Waste (CCW)** | **Constituent Concentration in Treated Waste TCLP Extract (CCWE)** |
| Mercury | 12 mg/kg[a] | 0.2 mg/L[b] |
| Total PCBs | 2 mg/kg | -- |

[b]mg/L = milligrams per liter
[c]mg/kg = milligrams per kilogram

## Table 3-2

### Storm Sewer Sediments Tube Furnace Summary

| Test | Time (min) | Oven Temperature (°C) | Recovered Hg (g) | Purge Rate (mL/min) | Initial Hg (mg/kg) | Final Hg (mg/kg) | TCLP Hg (µg/L) | Final PCB (mg/kg) |
|---|---|---|---|---|---|---|---|---|
| **Air Purge** | | | | | | | | |
| 1 | 10 | 450 | 2.72 | 100 | 42,458 | 104 | 11 | 7.3 |
| 2 | 20 | 450 | 2.58 | 100 | 42,458 | 95 | 8 | 0.2 |
| 3 | 10 | 550 | 2.79 | 100 | 42,458 | 72 | 5 | 0.1 |
| 12 | 20 | 550 | | 250 | 42,458 | 90 | NA | NA |
| 13 | 10 | 700 | | 300 | 42,458 | 54/61 (a) | NA | NA |
| **$N_2$ Purge** | | | | | | | | |
| 4 | 10 | 450 | 3.16 | 100 | 42,458 | 56 | 7 | 0.6 |
| 5 | 10 | 550 | 2.88 | 100 | 42,458 | 75 | 8 | 0.3 |
| **Steam Purge** | | | | | | | | |
| 6A | 10 | 450 | 2.73 | 270 | 42,458 | 52 | ND (2) | 0.2 |
| 7 | 15 | 450 | 2.36 | 470 | 42,458 | 86 | 10 | 0.1 |
| 8 | 20 | 450 | 3.12 | 470 | 42,458 | 82 | 8 | 0.2 |
| 9 | 10 | 550 | 2.68 | 545 | 42,458 | 62 | 10 | 1.5 |
| 11 | 10 | 550 | 3.12 | 633 | 42,458 | 59 | 11 | 0.3 |
| 10 | 15 | 550 | 2.44 | 643 | 42,458 | 63 | ND (2) | NA |
| 15 | 30 | 550 | | low | 42,458 | 91/71/62(a) | NA | NA |

(a) For these runs the bed was divided into 2 or 3 sections which were analyzed separately.
NA = Not analyzed.
ND = Not detected.

## Table 3-3

## Storm Sewer Sediments Tray Test Results Summary

| Test | Oven Temperature (°C) | Time (min) | | Air Purge (mL/min) | Final Hg (mg/kg) | Treated Soil Sample No. |
|---|---|---|---|---|---|---|
| | | At Oven Temperature | Total Run Length | | | |
| 1 | 550 | 10 | 30 | 100 | 113 | 1125-035-1R |
| 2 | 600 | 10 | 27.7 | 100 | 97 | 1125-036-1R |
| 3 | 650 | 10 | 26.8 | 100 | 97 | 1125-037-1R |
| 4 | 700 | 10 | 28 | 100 | 72 | 1125-038-1R |
| 4A | 550 | 10 | 27 | 100 | 100(b) | 1125-039-1R |
| 5 | 550 | 20 | 32.9 | 400 | 126 | 1125-043-1R |
| 6 | 550 | 40 | 54 | 400 | 99 | 1125-044-1R |
| 7 | 550 | 60 | 73.86 | 400 | 85 | 1125-045-1R |
| 8 | 550 | 90 | 102.7 | 400 | 113 | 1125-046-1R |

(b) Retreated residue from Test # 4 in an effort to further lower Hg.

## Table 3-4

## DARA Soils Tray Test Results Summary

| Test | Oven Temperature (°C) | Time (min) | | Residual PCBs (mg/kg) | Sample No., Treated Soil Description |
|---|---|---|---|---|---|
| | | At Oven Temperature | Total Run Length | | |
| 1 | 550 | 5 | 19.5 | ND (0.04) | 1125-074-1R, Center area is dark surrounded by lighter brown color area. |
| 2 | 500 | 10 | 25.8 | ND (0.04) | 1125-075-1R, Center area is almost charred. |
| 3 | 500 | 5 | 20.3 | ND (0.04) | 1125-076-1R, Center area is dark, almost charred surrounded by darker area than in Test 1. |
| 4 | 425 | 20 | 31.3 | ND (0.04) | 1125-077-1R, Center area is dark. |
| 5 | 425 | 10 | 24.25 | ND (0.04) | 1125-078-1R, Center dark area and the remaining area has dark green color. |
| 6 | 500 | 10 | 23.7 | ND (0.04) | 1125-079-1R, Center area is dark and the remaining area has a medium brown color. |
| 7 | 425 | 10 | 24.8 | ND (0.04) | 1125-080-1R, Center area is dark and the remaining area has dark brown color. |
| 8 | 500 | 0 | 14.7 | ND (0.04) | 1125-081-1R, Center area is dark and the remaining area has dark brown color. |
| 9 | 350 | 20 | 35.2 | 0.49 | 1125-082-1R, Center area is slightly dark. |
| 10 | 350 | 10 | 26 | 0.87 | 1125-083-1R, Center area is dark and the remaining area has dark brown color. |
| 11 | 425 | 5 | 18.3 | ND (0.04) | 1125-084-1R, Center area is slightly dark. |
| 12 | 350 | 5 | 21.2 | 1.0 | 1125-085-1R, Center area is dark. |
| 13 | 425 | 0 | 14.2 | 0.19 | 1125-085-1R, A large dark center area that includes one side of the tray. |

ND = Not detected.

## Table 3-5

## Storm Sewer Sediments RTA Test Summary

| Parameter | Untreated Soil | Run # 1 | Run # 1 Duplicate | Run # 2 | Run # 2 Duplicate |
|---|---|---|---|---|---|
| Test Temperature (°C) | | 600 | 600 | 350 | 350 |
| Time at Temperature (minutes) | | 10 | 10 | 10 | 10 |
| Total Test Time (minutes) | | 52 | 54 | 40 | 40 |
| Purge Media | | Air | Air | Steam | Steam |
| Purge Rate (l/min) | | 1860 | 1830 | 2950(a) | 2960(a) |
| Initial Soil Weight (g) | | 905.75 | 896.51 | 926.59 | 889.11 |
| Treated Solids Weight (g) | | 815.78 | 806.92 | 852.16 | 817.69 |
| % Weight Reduction | | 9.9 | 10 | 8.0 | 8.0 |
| Final Scrubber Water (g) | | 464.32 | 463.42 | NA | NA |
| Recovered Mercury (g) | | 58.01 | 33.13 | 30.60 | 28.92 |
| **Soil Analysis** | | | | | |
| Hg in Treated Soil (mg/kg) | | 82 | 141 | 3700 | 4100 |
| TCLP Hg (ug/L) | | ND@2 | ND@2 | ND@2 | ND@2 |
| PCBs (ug/kg) | | ND@33 | ND@33 | 2510 | 3200 |
| TOC (ug/kg) | | NA | NA | > 15800 | NA |
| | | | | | |
| | | | | | |
| **Condensate Analysis** | | | | | |
| Hg (mg/L) | | 371 | 94 | 151 | 427 |
| TCLP (mg/L) | | | | | |
| PCBs (mg/L) | | 2.4 | 0.3 | 1.2 | 1.3 |
| TOX (mg/L) | | | | 108 | |
| Total Uranium (pCi/L) | | | | 390 | |
| O & G (mg/L) | | | | 696 | |

(a) Calculated based on condensate recovery.

## Table 3-6

## DARA Soils RTA Test Summary

| Parameter | Untreated Soil | Run # 1 | Run # 1 Duplicate | Run # 2 | Run # 2 Duplicate |
|---|---|---|---|---|---|
| Test Temperature (°C) | | 450 | 450 | 400 | 400 |
| Time at Temperature (minutes) | | 10 | 10 | 5 | 5 |
| Total Test Time (minutes) | | 28 | 26 | 23 | 23 |
| Purge Media | | Air | Air | Air | Air |
| Purge Rate (l/min) | | 1000 | 1000 | 1000 | 1000 |
| Initial Soil Weight (g) | | 800 | 800.1 | 800.4 | 800.1 |
| Treated Soil (g) | | 674.5 | 675.4 | 678.2 | 677.4 |
| % Weight Reduction | | 15.7 | 15.6 | 15.3 | 15.3 |
| Final Scrubber Water (g) | | 599.1 | 618.7 | 605.9 | 611.1 |
| Recovered Organics (g) | | 0.8 | 0.9 | 2.4 | 2.9 |
| **Soil Analysis** | | | | | |
| Hg in Soil (mg/kg) | 1.1 | ND (0.1) | ND (0.1) | ND (0.1) | ND (0.1) |
| TCLP Hg ($\mu$g/L) | | ND (2) | | ND (2) | |
| PCBs (mg/kg) | 75 | 3.0 | 0.6 | 2.9 | 2.3 |
| TOC (mg/kg) | | | 14,500 | | |
| Total Uranium (pCi/g) | | | | 33.9 | |
| O & G | 5950 | | ND (500) | | |
| **Condensate Analysis** | | | | | |
| Hg (mg/L) | | | 0.03 | | 0.01 |
| TCLP ($\mu$g/L) | | | | | |
| PCBs (mg/L) | | 0.2 | 0.4 | 0.3 | 0.2 |
| TOX (mg/L) | | | | | |
| Total Uranium (pCi/g) | | | | | |
| TOC (mg/L) | | | 580 | | |

**Figure 2-1**
**RTA Schematic**