EPA/540/R-98/500 April 1998

# SIMULTANEOUS DESTRUCTION OF ORGANICS AND

STABILIZATION OF METALS IN SOILS

Emerging Technology Report

By

Center for Hazardous Materials Research Pittsburgh, Pennsylvania 15238

Assistance Agreeement CR 819604-01-0

Project Officer

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| Simultaneous Destruction of Organics and  | 6. PERFORMING C  | RGANIZATION CODE  |
| Stabilization of Metals in Soils  |  |   |
| 7. AUTHOR(S)  | 8. PERFORMING C  | RGANIZATION REPORT NO.  |
| Stephen A Daff  |  |   |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS   | 10. PROGRAM ELE  | MENT NO.  |
| Center for Hazardous Materials Research   |  |   |
| 320 William Pitt Way  | 11. CONTRACT/GF  | RANT NO.  |
| Pittsburgh, PA 15238  | CR 819   | 604-1   |
| 12. SPONSORING AGENCY NAME AND ADDRESS  | 13. TYPE OF BEPC   | BT AND PEBIOD COVERED   |
| National Risk Management Research Lab   | Project Rep  | ort 9/93-9/96   |
| Office of Research and Development  | 14. SPONSORING   | AGENCY CODE   |
| U.S. Environmental Protection Agency  | EPA  | /600/14   |
| Cincinnati, Ohio 45268  |  |   |
| Project Officer: Randy A. Parker (513)  | 569-7271 Reproduced best availab   | from<br>le copy.  |
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| 18. DISTRIBUTION STATEMENT  | 19. SECURITY CLASS (This Report)   | 21. NO. OF PAGES  |
|   | Unclassified   | 78  |
| Release to Public   | 20. SECURITY CLASS (This page)   | 22. PRICE   |
|   | Unclassified   |   |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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The U.S. Environmental Protection Agency through its Office of Research and Development funded the research described here under Assistance Agreement CR 819604-01-0 to the Center for Hazardous Materials Research. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document.

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This publication has been produced as part of the Laboratory's strategic longterm research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

> E. Timothy Oppelt, Director National Risk Management Research Laboratory

# ABSTRACT

The Center for Hazardous Materials Research (CHMR), through a Cooperative Agreement with the U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory (now the National Risk Management Research Laboratory), conducted a laboratory evaluation of the Sulchem Process for treatment of soils contaminated with organic hydrocarbons and heavy metals.

The Sulchem Process reacts the material being treated with elemental sulfur at elevated temperatures in an inert reactor system. Organic hydrocarbons react with the sulfur to form an inert fine solid of carbon and sulfur, hydrogen sulfide gas, and modest amounts of carbon disulfide. Heavy metals react to form sulfides or sulfide coated particles which are less soluble. The acid gases formed may be scrubbed or treated to recover elemental sulfur using an auxiliary process unit.

Various types of batch reactors were evaluated in the laboratory test program to establish process conditions and evaluate several reactor configurations. Processing temperatures of 250° to 350°C are required to obtain sufficient conversion in reasonable processing times. At these temperatures, hydrocarbons with boiling points greater than 350°C are virtually completely destroyed in the process. Hydrocarbons with boiling points less than about 250° to 300°C desorb from the soils reactor before reaction temperature is reached. Several alternatives were examined for treating the lighter organics including passing the vapors through a second stage reactor with sulfur vapor/liquid as well as collecting the organics in the condensate for alternative treatment. The latter configuration is the process equivalent of a reactive desorber which has a lower operating temperature.

Tests were employed using a contaminated soil sample from a manufactured gas plant (MGP) site. Destruction and removal efficiencies for aromatic hydrocarbons from phenanthrene to benzopyrene were all in excess of 99%.

Immobilization of heavy metals was determined by the concentration of the metals in the leachate produced by the EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), in which the metal concentration is compared to the EPA TCLP regulatory limits. Cadmium, copper, lead, nickel and zinc were found to provide significant reduction in the TCLP values following treatment of the soil by the Sulchem process. Copper TCLP values were reduced most effectively by this treatment. Lead TCLP values were reduced below regulatory targets when concentrations in the original soil were below about 10,000 ppm. Cadmium TCLP values were reduced below TCLP limits when the concentration in the original soil was below several thousand ppm.

Process economics for remedial soil treatment were estimated to be in the range of \$105 to \$181/ton depending on the size of the site and the processing rate.

This report was submitted in fulfillment of Assistance Agreement CR 819604-01 by the Center for Hazardous Materials Research under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 1993 to September 1996, and work was completed as of September 1997.

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# ABBREVIATION AND SYMBOLS

| A<br>BP | pre-exponential Arrhenius reaction constant |
|---------|---|
| CHMR    | Center for Hazardous Materials Research     |
| F       | activation energy                           |
| FID     | flame ionization detector                   |
| GAC     | granular activated carbon                   |
| GC      | gas chromatograph                           |
| ICP     | inductively coupled plasma                  |
| ID      | internal diameter                           |
| k       | rate constant                               |
| MGP     | manufactured gas plant                      |
| mL      | milliliter                                  |
| MS      | mass spectrometry                           |
| PCB     | polychlorinated biphenyls                   |
| R       | universal gas constant                      |
| SARM    | Standard Analytical Reference Matrix        |
| SS      | stainless steel                             |
| SSM     | Synthetic Soil Mixture                      |
| t       | reaction or residence time                  |
| Т       | temperature                                 |
| TCLP    | Toxicity Characteristics Leaching Procedure |

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# ACKNOWLEDGMENTS

The Center for Hazardous Materials Research (CHMR) would like to acknowledge the cooperation received throughout the project from the U.S. Environmental Protection Agency, Office of Research and Development. In particular, we would like to thank Mr. Randy A. Parker, from the EPA's Superfund Technology Demonstration Division who provided helpful guidance for this project.

CHMR would like to acknowledge the following individuals from the research team who were responsible for important contributions to this project.

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# 1.0 INTRODUCTION

In November 1992, the U.S. Environmental Protection Agency (EPA) Risk Reduction Engineering Laboratory (RREL) awarded the Center for Hazardous Material Research (CHMR) an Assistance Agreement (CR 819604-01-0) to test and evaluate the Sulchem Process. The Assistance Agreement was provided under the Emerging Technologies Program, E05 Solicitation. This report documents the results of this study. Prior reports are referenced [1,2,3,4].

# 1.1 SULCHEM PROCESS

The basis for the Sulchem technology is a family of interrelated processing technologies described in a series of four issued patents (U.S. Patent Nos. 4,581,442, dated April 8, 1986; 4,921,936, dated May 1, 1990; 4,990,404, dated February 5, 1991; and 5,347,072, dated July 13, 1994) and one patent pending, (Harold W. Adams, inventor), collectively referred to here as the Sulchem technology.

The Sulchem technology works by reacting elemental sulfur with waste materials in an oxygen-free environment. In the original patents, the reactions of the sulfur were with pure organic mixtures in either the liquid (typically at 250°C to 350°C) or vapor phase (typically at 500°C). The products are primarily hydrogen sulfide and an inert black solid of approximate formula  $CS_{0.56}$  [5].

This research and development focussed on the application of the Sulchem Process to contaminated soils at Superfund sites. The Sulchem Process was anticipated to provide destruction of hazardous organics while simultaneously stabilizing metals in contaminated soils. The Sulchem Process uses elemental sulfur, which reacts with the carbon in organic materials at moderately elevated temperatures to form an insoluble, inert carbon-sulfur amorphous solid ( $CS_{0.56}$ ) The contained heavy metals are immobilized through formation of insoluble metal sulfides.

The Sulchem Process's main process components include:

- A pre-reaction mixer where the soil and sulfur are mixed;
- An externally heated rotating solids reactor;
- A vapor phase reactor where desorbed organics from the first reactor are further reacted with elemental sulfur;
- The off-gas handling system, which collects and treats condensable by-products and scrubs acid gases from the effluent vapors; and
- A post-reaction treatment unit that recovers excess reagent and prepares the treated product to comply with on-site disposal requirements.

A general block flow diagram for the Sulchem Process is shown in Figure 1. The Sulchem Process, as applied to treatment of soils and sludge, consists of two reactors, one for treating the solid phase material and a second for treating the gases emitted from the first reactor, including desorbed organic vapors.

# FIGURE 1. SULCHEM PROCESS SCHEMATIC



2

The second reactor is required because, for the more volatile organic compounds, desorption effectively competes with reaction with liquid phase sulfur. The details of the integration between these two reactor stages will be discussed in subsequent sections.

The feed soil, possibly after some dewatering, is fed into a pre-reaction mixer where elemental sulfur (and other reagents, if used) are added to the feed soil and lightly mixed. The feed mixture (soil and reagents) is next fed to the first reactor which consists of an indirectly heated, rotary reactor. A controlled atmosphere is provided in the reactor with flow of inert gases over the tumbling solids excluding oxygen from the reactor and removing off-gases released by the process. Heat up, reaction, and cool down zones for the reactor will be employed as the solids move through the reactor.

#### 1.2 PRIOR WORK

The National Environmental Technology Applications Center (NETAC), an affiliate of CHMR, previously constructed and operated a pilot-scale production unit of the Sulchem technology [5]. The unit enabled the collection of steady-state samples of the reaction products and by-products for subsequent analysis. The results demonstrated the application of the Sulchem technology to destroy organic compounds in a vapor phase reaction with sulfur. The organic compounds tested in these vapor phase pilot tests included perchloroethylene (PCE), trichloroethylene (TCE), trichlorobenzene, Freon 113, and Aroclor<sup>®</sup> 1242.

Exploratory screening tests were conducted using simulated contaminated soil to test the reactivity of sulfur with some of the typical heavy metals encountered in hazardous waste. These tests were designed to determine if the sulfur reaction with heavy metals immobilized the metals sufficiently to pass the TCLP (Toxicity Characteristics Leaching Procedure) test. A small-scale batch test was run on an EPA Synthetic Soil Matrix (SSM) spiked with arsenic, chromate, lead, and ferric ferrocyanide (as a complex cyanide). The results demonstrated reduction of TCLP leachate values from 6 and 35 mg/L for arsenic and lead, respectively, to below RCRA regulatory levels (1 and 5 mg/L, respectively) [6].

Based on these separate demonstrations of the ability of the Sulchem Process to destroy organics in the vapor phase, and initial tests to immobilize metals in soils using liquid phase sulfur, CHMR prepared the proposal to the EPA Emerging Technologies program. The proposal was to evaluate the process conditions necessary to both destroy organics and immobilize metals in one process and to establish the limits for this process on these different contaminants. That objective thus became the basis for the project being reported here.

Concurrent with this project, a privately funded treatability test was made of the Sulchem Process in both closed and vented mode batch reactors [10]. The samples tested were two variations on a soil blend (prepared according to Section 3.2) containing 1.70% cadmium, 1.90% mercury, 1.47% zinc and 750 ppm of Aroclor<sup>®</sup> 1260. PCB destruction efficiency varied from 99.0 to 99.95% for runs ranging from 275 to 350°C. TCLP metals met RCRA standards for mercury and indicated 95% reduction for TCLP cadmium and zinc TCLP reduction of 42 to 99.4% depending on soil type and process conditions.

# **1.3 PROJECT OBJECTIVES**

The purposes of this project were to determine the technical and economic feasibility of using the Sulchem Process for site remediation. Therefore, the specific objectives for this project were as follows:

- Establish that both organic compound destruction and heavy metals immobilization can be carried out simultaneously;
- Establish the limits of applicability for destruction of different organic compounds in processing soils, sludge and sediments;
- Establish the limits of applicability for different heavy metals in processing soils, sludge, and sediments for heavy metal stabilization;
- Establish processing conditions to achieve organic compound destruction and heavy metal stabilization;
- Determine the chemical/mineralogical mechanism for the stabilization of heavy metals in soil matrices;
- Establish process requirements for post-reaction treatment of the raw reactor product (solids) as well as the off gases/condensate produced;
- Develop process economics for the Sulchem Process for treatment of soils, sludge, and sediments; and
- Make recommendations concerning further development of the Sulchem Process.

# 2.0 EQUIPMENT AND EXPERIMENTAL PROCEDURES

Three types of reactor systems were used in the experimental program. The initial screening tests of soils were performed in three variations of small batch reactors. Subsequently, a vapor phase reactor was used to evaluate a second stage reactor in the process whereby unreacted organic vapors emerging from the soils reactor was simulated as feed to a vapor reactor. Finally, an integrated reactor system was used to evaluate the overall process performance in a larger batch reactor.

The following section includes a brief summary of sulfur properties at typical reaction temperatures. Subsequent sections describes the reactor systems used and the general operating procedures employed in the test runs with each of these reactor systems.

#### 2.1 SULFUR PROPERTIES

Elemental sulfur is used as the chemical reagent in the Sulchem Process. Sulfur is an oxidizer, with properties similar to that of oxygen, particularly at temperatures above 250°C. Key parameters which are important to understand the behavior of sulfur and its use in the Sulchem Process include its melting point, liquid viscosity, boiling point, autoignition temperature, and the temperature at which it exhibits oxidative behavior in the presence of organics.

The melting point for sulfur is approximately 120°C. Sulfur melts to form a viscous liquid, with viscosity of approximately 120 cP. The viscosity drops with the temperature as the temperature rises to 160°C  $\mu = 67$  cP). Then the viscosity anomalously increases to approximately 93,000 cP, forming a practically unflowable liquid. Above 187°C, the viscosity decreases again with temperature, dropping to 15,000 cP at 250°C, and to below 1,000 cP at about 300°C [7]. The "viscous region" for liquid sulfur presents problems when designing or building a sulfur heating system, as the highly viscous sulfur resists heat transfer.

The boiling point for liquid sulfur is 444°C, which provides an upper bound for temperature for a liquid sulfur reactor system. The autoignition temperature of sulfur is approximately 230-260°C although open cup flash points of 187-207°C have been reported [8]. The literature indicates that sulfur begins to undergo relatively fast reactions with hydrocarbons, causing the evolution of hydrogen sulfide gas, at temperatures as low as 180°C [8], although previous Sulchem work suggested that a significant sulfur/hydrocarbon reaction does not begin until temperatures of approximately 220-240°C [5].

When sulfur reacts with a hydrocarbon, two principal products are formed: hydrogen sulfide gas ( $H_2S$ ), and an amorphous carbon-sulfur solid, having the approximate formula of  $CS_{0.56}$ . Previous work showed that the reaction proceeds both in the vapor and liquid phases.

#### 2.2 BATCH REACTORS

Three different small batch test reactors were employed for the initial screening studies. Each was sized to heat batches of approximately 200 g of soil in an inert atmosphere from ambient temperature to nominal reaction temperatures ranging from 250° to 450°C.

For the initial tests, two unstirred reactors were employed. One of these was designated as the closed mode reactor (high pressure) and the other the vented mode reactor (low pressure). These two reactors were heated by immersion in a heated fluidized sand bath. Subsequently, an autoclave was modified to provide an auger mixed reactor. The autoclave was heated with a cylindrical furnace jacket which could be lowered after the run for rapid cooling of the reactor. The following briefly describes these three reactor systems and the general experimental procedures followed.

#### 2.2.1 Closed Mode Reactor

The closed mode reactor consisted of a high pressure bomb approximately 10" long and 1-3/8" I.D. (nominal internal volume approximately 270 mL) made of 304 SS. The bomb was fitted with an internal thermowell along the center axis and was equipped with a pressure gauge and shut-off valve. After filling with the reaction mixture, the bomb was leak tested and inserted into a heated fluidized sand bath.

After cooling, the excess gas was bled through a bubbler flask of 10N NaOH to absorb the H2S and into a gas burette to measure the volume of non-condensable gases. The quantity of H2S was measured by weight gain of the caustic flask. After the gases were removed and measured, the bomb was opened and the solid residue removed and weighed.

#### 2.2.2 Vented Mode Reactor

The vented mode reactor was made from a 2" I.D. 316 SS pipe and was operated at ambient pressure. The reactor was outfitted with an upper condenser section which permits sulfur and other higher boiling components to condense and reflux back to the reactor. The upper section was maintained between the melting point and viscosity limit for molten sulfur (i.e., 120° to 150°C).

The reactor section was approximately  $7\frac{1}{2}$ " long and welded to a 2" flange. The flange was attached to an upper section of the reactor approximately 12" long and containing an internal coil of  $\frac{1}{4}$ " SS tubing. The reactor was heated by immersing the lower section and the flange in the fluidized sand bath. The upper section was heated by both external heating tape and by circulation of hot oil through the coil to keep this zone at 120°C to 150°C. Off-gas from the condenser section was passed through a heated line to an ice trap and then a 10N NaOH bubbler.

The initial experiments involved shakedown and redesign of the vented mode reactor system. These experiments included testing use of hot water for the condenser section, which was subsequently replaced with a hot oil (  $\sim 150$  °C) circulating system.

#### 2.2.3 Stirred Reactor

Initial tests with the above two reactors, which lacked any means of mechanical stirring, demonstrated that the segregation of the reactants occurred during heating due to the sulfur melting and collecting at the bottom of the reactor. Therefore, there was the possibility that for runs below the boiling point of sulfur the soil in the upper part of the reactor might not have sufficient opportunity to react with either sulfur vapor or sulfur liquid. A stirred batch reactor would better simulate the expected continuous reactors employed on larger scale than an unstirred

reactor. Secondly, there was a concern in using the closed mode reactor that there might be pressure effects on either the reaction (due to the high molecularity of gaseous products) or on the formation of the stabilized treated soil product. Consequently, a stirred, vented mode reactor was employed for the subsequent experimental runs.

The reactor was a standard Autoclave Engineers stirred 1-liter autoclave made of 316 SS. The autoclave is rated for 9000 psi although it was used at ambient pressures for these experiments. A 5-inch high auger was installed on the stirrer shaft, which left approximately ¼ " space next to the wall that was not stirred. The auger was slowly turned during the experiment with an air drive. A thermowell was located between the wall and auger near the bottom of the reactor. A second thermowell was located in the vapor space of the reactor. A cooling coil was located in the upper portion of the reactor zone, but was not used during the experiments. The autoclave reactor is illustrated schematically in Figure 2.

The vent line from the autoclave was attached to a small stainless steel dip-tube trap. The connecting line was heated with heating tape and the trap was cooled in ice water. In later experiments when recovery of unreacted organic compounds was being determined, this single trap was replaced with two traps in series for more efficient trapping.

The effluent gas from the trap was connected to a 10*N* NaOH bubbler as before. The non-condensable gases were vented to the hood. For some experiments, the volume of non-condensable off-gas produced over measured time intervals was determined by collection over water in a gas burette. No analyses of these gases were made during this project although previous work in this laboratory [5] has shown the minor amount of non-condensable gaseous product formed was primarily hydrogen, in addition to the nitrogen used for purge gas.

#### **2.2.4 Batch Reactor Experimental Procedures**

The following outlines the general operating procedures for the batch reactor runs.

Weighed quantities of soil blend material used for each experiment were determined as well as the weights of sulfur and other reagents, if any. The initial tare weights of the caustic scrubber (including solution) was also determined prior to each run.

At the conclusion of each experimental run and after cool down to room temperature, the caustic scrubber was removed and weighed. The weight gain was attributed primarily to neutralized hydrogen sulfide. The ice trap was weighed and the collected liquid removed. Following rinsing of the trap with solvent, and then acetone and drying, the tare weight of the trap was determined. The weight of condensate was calculated by difference.

The reactor was then disassembled and the raw reactor solids (generally a dark gray powder) were removed from the reactor. A clean spatula and a clean small wire brush was used to remove residual solids (principally sulfur) from the auger and condenser coil of the reactor. For the lower temperature runs, sulfur crystals occasionally had to be chipped from the reactor with a small chisel. After all of the collected solids were removed, a total weight was determined and the mixture manually homogenized before sampling. The reactor equipment, including auger



and coil, as well as the tools used (spatula, brush, and chisel) were cleaned with water and detergent, rinsed with acetone and dried before reuse on the next run.

For those runs in which recovered organic compounds were determined, the reaction system hardware were separately rinsed with methylene chloride to remove and recover any residual organic compounds. Several separate rinses were used for the reactor including auger and coil which were saved for use in the Soxhlet extraction of the raw reactor solids sample. A volumetric fraction of these rinses, calculated from the weight ratio of the Soxhlet sample to the weight of total reactor solids, was used in the Soxhlet boiling flask. In this way, the Soxhlet extract was based on a representative sample of the raw reactor solids.

In addition, for the runs with organic compounds, all rinses of the connecting tubing and the ice trap were used in the liquid-liquid extraction of the ice trap condensate. Similarly, all of the rinses of the connecting tubing and caustic bubbler flask were also used in the liquid-liquid extraction of the caustic solution.

#### 2.3 VAPOR REACTOR

CHMR designed and constructed a vapor reactor test system. The reactor was a 316 SS vertical pipe (24" x 3" diameter) partially filled with molten sulfur and with gas fed through a sparger in the bottom of the reactor. The system was tested using toluene vapors as the organic feed. Toluene was chosen because it represents a volatile organic, anticipated to be vaporized in the soils reactor; it is an aromatic and expected to be less reactive than aliphatic compounds; and, it is well characterized and relatively easy to work with.

Nitrogen gas from a high pressure cylinder was split into three streams, each of which had the flow rate separately monitored. One stream was fed through a sparge tank, in which it became saturated or nearly saturated in toluene vapors. The second fraction bypassed the sparge tank, but was mixed with the effluent from the sparge system before being fed to the reactor. By controlling the ratio of the flows between these two streams, the toluene influent concentration was controlled. The third stream, typically on the order of 50 mL/min, was a nitrogen purge stream fed directly to the top of the reactor vessel. It was designed to reduce the likelihood of sulfur plugging in the vent to the reactor. The vapor residence time in the reactor was calculated by dividing the overall free volume in the reactor, which is the sum of the flow rates of the three nitrogen inlet streams.

The toluene/nitrogen mixture was passed into the reactor at the bottom of a bath of molten sulfur. The mixture passed into the sulfur, initially through a perforated plate sparger, which was later replaced with a 3/8" fine mesh screen, which CHMR believes produced smaller bubbles. Passing through the perforated plate or screen, bubbles form, and become saturated with sulfur as they pass through the molten sulfur. The organic compounds inside the bubbles reacted with sulfur in the vapor phase as the bubbles rose. Further reactions with the vapor would occur as the vapors pass through the top of the reactor.

The feed stream passed through the molten sulfur and out the top of the reactor. A splash guard near the reactor top protected against escape of liquid sulfur. The gases passed through two one-half inch stainless steel pipe traps, maintained at -20°C by periodically adding dry ice to ethylene glycol. Care was taken to avoid lower temperatures where H2S would condense (BP -42°C). These traps removed water vapor, sulfur, and residual organic vapors. The gases were next passed through a 10N NaOH scrubber to remove hydrogen sulfide before discharge through a vent.

The reactor was heated using Kelrod heaters, and maintained at the appropriate temperature using a combination of variacs on the heater units and an automatic temperature controller. The reactor was packed in glass wool insulation to reduce heat loss and help maintain constant and consistent skin temperatures. The off-gas system was heated with heat tape to the first ice trap to reduce sulfur condensation, which may clog the piping.

To determine the toluene feed to the system, the toluene sparge vessel was weighed before and after each experiment. To determine overall toluene destruction, the materials collected in the traps were weighed, extracted with methylene chloride, and analyzed for toluene after each experiment by GC-FID using a recovery standard. The weight change (gain) in the scrubber system was also noted.

# 2.4 ROTARY SOIL REACTOR

To test the full reactor system concept, CHMR designed and constructed a pilotscale rotary soil reactor. The soil reactor is shown in Figure 3. It consisted of two 316 SS cylindrical externally heated chambers, each of which was 8-inches in diameter and 12-inches long. The two chambers were separated by a metal flange with a two-inch opening in the center. The system was designed to rotate at 0 to 10 revolutions per minute (rpm). The reactor was heated using approximately 9,000 watts electrical heater (208V, 3-phase), controlled via a temperature controller which received as its input the internal soil temperature. The entire reactor system was maintained under anoxic conditions through the use of a nitrogen purge. The rotating reactor was connected on either side to a 2-inch piping which in turn was connected to a rotating union, which enabled the reactor to turn while the downstream and upstream piping and connections did not.

Soil mixed with sulfur was placed to the first chamber. Sulfur was added to the second. The first chamber was baffled along the horizontal axis with 2-inch baffles, to pick up and mix the soil /sulfur mixture. The second chamber was baffled vertically with 6-inch baffles, to hold up gases passing through it and to provide surface area for contact between the gas stream and the molten sulfur so as to facilitate reactions between the sulfur and organics in the vapor phase. The second stage reactor was designed to provide between three and five minutes residence time.

Nitrogen gas was fed to the first chamber, at between 1 and 2-L/min flow rate to maintain an oxygen-free chamber. The nitrogen purge gas picked up water vapor, volatile organics, hydrogen sulfide, elemental sulfur vapor and other volatile compounds. The purge stream passed through the soil reactor and into the sulfur reactor. Inside the sulfur reactor, which was heated to the same temperature as the soil reactor, sulfur reacted with some of the organic compounds volatilized from the soil. The purge stream passed through the sulfur reactor and out via a heated line to a series of traps, which were designed to condense the water vapor

FIGURE 3. ROTARY SOIL REACTOR.



and the volatile organics present in the gas stream. The first trap consisted of a 6-inch diameter closed 316 SS pipe, with a dip leg reaching to within 6 inches from the bottom. The trap was maintained in an ice bath at approximately 2°C. This trap collected the majority of the volatile compounds, particularly water vapor. The second trap was maintained using dry ice at -20°C. This trap collected the remaining water vapor, organics, and carbon disulfide.

The gas stream passed through the second trap and into a 4-L caustic scrubber, containing 10N NaOH. The scrubber removed hydrogen sulfide gas. The gas stream passed through this scrubber and was vented to the atmosphere-via a hood.

The reactor was operated in batch mode, similarly to the full-scale unit envisioned under this configuration. However, for a full-scale unit, the sulfur and soil sides would likely be separated, to enable independent control of the heating systems (to maintain the sulfur temperature) and to allow for isolation of either side should it be necessary.

# 2.5 DATA AND SAMPLE COLLECTION

All data and sample collection was performed in conformance with the approved project Quality Assurance Project Plan (QAPP), unless noted below.

# 2.5.1 Feed Characterization

Feed materials for the early runs consisted of spiked samples, made with reagent grade chemicals, to form standard soil mixtures. Larger scale tests employed field samples from a manufactured gas plant site, as described in Section 3.3. Samples of this material were analyzed using ultrasonic extraction (Method 3550) and GC/FID analysis (Method 8100). Duplicate samples of representative materials were analyzed to determine the feed soil concentrations. Duplicate FID runs were performed to determine the precision of the analytical procedure, which was found to be within the QAPP standard of  $\pm$  15% (see Appendix B). 1,2,4-trichlorobenzene was used throughout the experiments as an internal recovery standard.

# 2.5.2 Product Sampling

Products were collected from the traps, scrubber and reactor. All the material present in the traps was used in the extraction. If the scrubber contained less than 100 mL of material, then the entire contents of the scrubber were used in the analysis. If the scrubber contained more than 100 mL, then a 100 mL sample of the scrubber water was taken for analysis. For the small-scale tests, reactor samples included the entire reactor product. For the larger-scale tests, representative samples were by homogenizing the reactor contents in a Veeblender, then removing 5 mL from three different locations within the blended material.

# 2.5.3 Data Collection

Data such as temperature and pressure were read directly from the thermocouples or pressure gauges which were part of the equipment. Gas flow rates were determined using calibrated rotameters, and are reported at standard temperature and pressures (25°C and 1 atm) unless otherwise noted.

## 2.6 QUALITY ASSURANCE/QUALITY CONTROL

As noted, the project was conducted in conformance with an approved QAPP [2]. Critical measurements made during the process runs include the TCLP of the feed and products for runs involving heavy metal contaminated feeds. for runs involving organic contaminants, critical measurements included semivolatiles content of the feed, reactor product, and off-gases. The off-gas semi-volatile content was typically measured by summing the contributions from each component of the off-gas collection system, including the ice trap(s) and scrubber. Quantitative QA objectives for critical analyses for the project are noted in Table 1.

The two major QA objectives for the project were (1) to determine the input concentration and destruction efficiency of various semi-volatile organic compounds during process tests and (2) measure the TCLP leachability of the untreated and treated soil to determine whether or not the treated soil passed the TCLP leachability tests.

As specified in the QAPP, CHMR performed duplicate analyses of 10% of the critical analyses for samples taken using the rotary reactor. Duplicate analyses of the screening tests (performed using the vented stirred reactor) were not performed unless inter-experiment anomalies were noted. Results from select duplicate analysis performed as part of the quality assurance procedures are given in Appendix B.

Data reduction procedures primarily included summing the various components of product streams to determine destruction efficiency. Specific reduction methods are discussed in more detail in Section 5.

| Table 1. Quantitative QA Objectives                 |        |                   |   |                    |              |              |                  |  |
|---|--------|-------------------|---|--------------------|--------------|--------------|------------------|--|
| CRITICAL<br>MEASUREMENT                             | MATRIX | TCLP<br>REG. LIM. | METHOD                                  | DET. LIM<br>(mg/L) | PREC.<br>(%) | ACCU.<br>(%) | COMPLE<br>TENESS |  |
| Toxicity<br>Characteristics<br>Leaching Proced.     | S      |                   | Part 268,<br>Appendix I;<br>Method 1313 |                    |              |              |                  |  |
| Arsenic   | S      | 5 mg/L            | SW 7060<br>EPA 7000                     | .005               | ±15          | ±20          | 95               |  |
| Barium  | S      | 100 mg/L          | SW 6010<br>EPA 7000                     | .01                | ±15          | ±20          | 95               |  |
| Cadmium   | S      | 1 mg/L            | SW 6010<br>EPA 7000                     | .01                | ±15          | ±20          | 95               |  |
| Chromium  | S      | 5 mg/L            | SW 6010<br>EPA 7000                     | .02                | ±15          | ±20          | 95               |  |
| Lead  | S      | 5 mg/L            | SW 6010<br>EPA 7000                     | .05                | ±15          | ±20          | 95               |  |
| Mercury   | S      | .2 mg/L           | SW 7470<br>EPA 7000                     | .005               | ±15          | ±20          | 95               |  |
| Nickel  | S      | 5 mg/L            | SW 6010<br>EPA 7000                     | .02                | ±15          | ±20          | 95               |  |
| Semivolatile<br>Organic<br>Compounds<br>(examples): |        |                   | L:SW3510<br>S:3540/3550<br>Product:3660 |                    |              |              |                  |  |
| Naphthalene   | S/L    | NA                | SW8100                                  | .3 mg/kg           | ±15          | ±20          | 90               |  |
| Anthracene  | S/L    | NA                | SW8100                                  | .3 mg/kg           | ±15          | <u>±2</u> 0  | 90               |  |
| Trichlorobenzene                                    | S/L    | NA                | SW8100                                  | .3 mg/kg           | ±15          | ±20          | 90               |  |
| Volatile Organic<br>Compounds<br>(examples):        |        |                   | L:SW3510<br>S:3540/3550<br>Product:3660 |                    |              |              |                  |  |
| Toluene   | S/L    | NA                | SW8010/<br>8020                         | 5 ug/kg            | ±15          | ±20          | 90               |  |
| Xylene -  | S/L    | NA                | SW8010/<br>8020                         | 5 ug/kg            | ±15          | ±20          | 90               |  |
| Tetra-<br>chloroethylene                            | S/L    | NA                | SW8010/<br>8020                         | 5 ug/kg            | ±15          | ±20          | 90               |  |

-SW refers to "Test Methods for Evaluating Solid Waste." SW-846, Third Edition.

# 3.0 SOIL SAMPLES

The initial screening tests employed several standard soil mixtures which were used to prepared various spiked mixtures for use in individual laboratory tests. A field sample was obtained for the larger scale process tests. The characterization of these various test mixtures and samples used in the project are discussed in this section.

# 3.1 SARM SAMPLES

One set of test soil blends used in this project were the SARM-II and SARM-III samples prepared by EPA and Enviresponse, Inc. The SARM samples are based on the same SSM soil blend (discussed below) that has had a number of heavy metal and organic compounds (both volatiles and semivolatiles) added. The SARM samples had been prepared by addition of: arsenic trioxide ( $As_2O_3$ ), cadmium sulfate ( $CdSO_4$ ), chromium nitrate ( $Cr(NO_3)_3$ ), copper sulfate ( $CuSO_4$ ), lead sulfate ( $PbSO_4$ ), nickel nitrate ( $Ni(NO_3)_2$ ), and zinc oxide (ZnO).

For the purpose of the initial screening experiments on metal stabilization, the SARM-III sample was used only to study the stabilization of the contained heavy metals. No analyses of the contained organic compounds were made on the products from the SARM-III runs.

## 3.2 SPECIAL SOIL BLENDS

Most of the experiments were performed on synthetically prepared soil blends containing weighed quantities of heavy metals or semivolatile organic compounds specifically added for each series of experiments. Two different soil blends were used in this experimental program as the starting materials from which the heavy metal and organic spiked samples were prepared.

One of the soil blends used in this work was the EPA Synthetic Soil Matrix (SSM) prepared and distributed by Foster Wheeler Enviresponse, Inc. of Edison, NJ. This material is the *unspiked* blend used to prepare the SARM and SSM samples. This material was supplied in a 55 gal drum. Fresh samples were prepared by spreading approximately 1 to 2 kg in a shallow pan to air dry overnight. After drying, the soil was screened with a 9 mesh screen to remove oversized material. The screened sample was stored in screw top glass jars.

Combustion tests on the SSM material, after acidifying to remove carbonate carbon, indicated a total organic carbon content (TOC) of 0.5% or less. It is well known that the capacity of soils to adsorb semivolatile organic compounds relates to the organic carbon content. Accordingly, a second soil blend was prepared and used for most of the test program. The second soil blend consisted of 75% by weight of the SSM soil described above and 25% by weight of horticultural topsoil. Each of these two materials were dried overnight by spreading the material in a shallow pan. Each dried soil was separately screened to remove oversize material with a 9 mesh screen and stored in screw top glass jars.

One kilogram samples were prepared by weighing out the dry soil blend components, as well as the added spike materials, and placing them in a screw top quart glass jar. The mixture was vigorously blended by shaking and rotation of the closed jar. In other cases, larger samples were prepared using a commercial laboratory-size Vee blender.

# 3.3 MANUFACTURED GAS PLANT SAMPLE

A manufactured gas plant (MGP) sample was obtained from a utility in upstate New York. The sample was obtained from a storage pile and was selected by the utilities's contractor to be a heavily contaminated sample. Approximately 15 gallons of the material were obtained from the site. The soil was dark brown, with a strong "coal tar" odor, and obvious small chunks of tar.

A MGP sample was selected for the larger scale rotary soil reactor runs since these sites typically have high levels of higher boiling aromatics hydrocarbons but very little VOCs. There are also over 1500 manufactured gas plant sites across the country. It was therefore felt to be an appropriate test feed for demonstrating performance of organics destruction in the Sulchem Process.

| Table 2. Characterization of MGP Sample               |  |  |  |  |  |  |
|---|--|--|--|--|--|--|
| Moisture  | 20.1%  |  |  |  |  |  |
| Total Extractable Organics                            | 2.8%   |  |  |  |  |  |
| Particle Size Distribution                            | <4 mesh: 51.1%<br>4-10 mesh: 20.7%<br>10-20 mesh: 14.7%<br>20-60 mesh: 11.2%<br>>60 mesh: 2.2%                         |  |  |  |  |  |
| $\begin{tabular}{lllllllllllllllllllllllllllllllllll$ | 1253 μg/g<br>423 μg/g<br>623 μg/g<br>1626 μg/g<br>1343 μg/g<br>605 μg/g<br>30 μg/g<br>543 μg/g<br>366 μg/g<br>256 μg/g |  |  |  |  |  |

Table 2 summarizes the characterization of the MGP sample:

The organic hydrocarbons present in the MGP soil sample were determined by extraction and GC/MS employing a variation of Method 8270 used in this laboratory for quantifying petroleum degradation found in bioremediation product evaluation [9]. This method determines alkanes from  $C_{10}$  to  $C_{35}$  and various polycyclic aromatic hydrocarbons including totals for mono-, di-, and tri-methyl derivatives based on the sensitivity of the unsubstituted homolog.

The hydrocarbons found ranged in boiling point from methyl naphthalenes to benzopyrenes. The major compounds were methyl naphthalenes (mono, di and trig phenanthrene, pyrene and other similar polycyclic aromatic hydrocarbons including the alkylated homologs. The only other major hydrocarbons observed were pristane, phytane and several analogs ( $C_{18}$  to  $C_{21}$ ). Minor amounts of higher n-alkanes were also present. The major compound classes found in this sample

and quantified by the GC/MS method used, for which standards were available, are summarized in Table 2.

Several samples of the MGP soil were also oven dried and air dried at room temperature for two of the test runs to evaluate the effect of moisture level. Moisture contents of these separate feed samples were also determined.

#### 4.0 ANALYSES

This Section references the standard methods used for the analyses performed for the test runs for these projects. These include measurement of the organics in the test blends, as well as the MGP test samples, and comparison with the organics recovered form the reactor and associated traps to determine organics destruction. In addition, metal stabilization was determined and compared to the metal spiked feed test soils and compared with the raw reactor solids product.

#### 4.1 ORGANIC ANALYSES

In the experiments where destruction and removal of organic compounds were studied, separate extractions were made of the raw reactor solids, of the ice trap condensate, and of the caustic scrubber solution. These extractions, along with rinsings of the appropriate equipment, were made in order to determine the quantity of any unreacted, or desorbed/distilled, organic compounds from the reaction products or equipment hardware.

Most of the hydrocarbon and chlorohydrocarbons used for these tests were semivolatile organics and were analyzed by gas chromatography outfitted with flame ionization detector (GC-FID) and chemical assignments confirmed by gas chromatography-mass spectrometry (GC/MS). The standard EPA analytical methods employed for these tests are listed in Table 3.

#### 4.2 METALS ANALYSES

For those experiments in which metals stabilization was being tested, samples of the soil blend used, as well as the raw reactor solids product were analyzed by the Toxicity Characteristics Leaching Procedure [(TCLP) - EPA Method 1311]. (see Table 3) Following acid digestion (Method 3005), the leachate was analyzed by Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy (Method 6010) for the test metals which included: arsenic, barium, cadmium, chromium, cobalt, copper, lead, nickel, and zinc.

#### 4.3 OTHER ANALYSES

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Mineralogical testing and speciation was employed using optical microscopy, X-ray diffraction, and scanning electron microscopy with energy selection detection.

| Table 3. Analytical Methods         |                                     |  |  |  |  |  |
|-------------------------------------|-------------------------------------|--|--|--|--|--|
| Type of Analysis                    | Methods                             | Samples  |  |  |  |  |
| ORGANICS DESTRUCTION                | N                                   |  |  |  |  |  |
| Extraction                          | Soxhlet (3540)<br>Sonication (3350) | soil feed<br>raw reactor solids                                    |  |  |  |  |
|                                     | Liquid-Liquid (3510)                | condensate<br>scrubber_solution                                    |  |  |  |  |
| Clean-up                            | Sulfur removal (3660)               | raw reactor solids<br>condensate<br>scrubber solution              |  |  |  |  |
|                                     | Florisil column<br>(3620)           | soil feed<br>raw reactor solids                                    |  |  |  |  |
| Gas Chromatography                  | FID (8100)<br>GC/MS (8270)          | soil feed<br>raw reactor solids<br>condensate<br>scrubber solution |  |  |  |  |
| METALS IMMOBILIZATION               | N                                   |  |  |  |  |  |
| TCLP                                | Method 1311                         | soil feed<br>raw reactor solids                                    |  |  |  |  |
| ICP Atomic Emission<br>Spectroscopy | Method 3005<br>Method 6010          | soil feed<br>raw reactor solids                                    |  |  |  |  |
| Moisture                            | Oven drying                         | soil feed  |  |  |  |  |
| Particle size<br>distribution       | Microtrac analysis                  | soil feed  |  |  |  |  |
| Total extractable organics          | Method 3550                         | soil feed<br>reactor feed  |  |  |  |  |

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# 5.0 ORGANICS DESTRUCTION

The Sulchem Process is conceived to be a two-stage process in which the soil is reacted with sulfur in the first stage. Unreacted organics desorbed from the first stage react with sulfur in the vapor phase in the second stage. In this Section, preliminary tests of organic destruction in the soil reactor and in the vapor reactor are reported.

The purpose of these tests were: (1) to establish the soil treatment temperatures and other process conditions necessary to achieve organic compound destruction in the soil reactor; (2) to estimate the boiling range of volatile organics that will be desorbed during heat up of the soil reactor before reaction temperatures are reached; and (3) to evaluate process conditions for a second stage vapor reactor to treat the volatile organics desorbed from the soil reactor.

## 5.1 SOIL BATCH REACTOR TESTS

In batch reactor tests of the reaction mixture, the soil and sulfur are heated, while mixing, from ambient temperature to the desired reaction temperature and then held at the run temperature for the desired time interval. The temperature at which significant reaction first occurs was estimated, based on small batch tests with mineral oils in the closed and vented mode reactors, to begin in the range of 200°C to 250°C for the more reactive saturated hydrocarbons. Therefore, the initial screening tests were run at temperatures of 250°C and higher.

A comparison of the boiling range of the organics in the feed soil with the boiling range of the desorbed vapors collected in downstream traps indicated the approximate temperature range over which desorption and reaction compete in the solids reactor. For example, those compounds with high recoveries in the overhead represent the boiling range where desorption takes place before any reaction occurs. Those compounds not found in the overhead represent the boiling range above the reaction temperature regime. An intermediate boiling point regime, where only partial recovery is found, represents the boiling range where reaction and desorption processes compete.

Therefore several scoping tests were performed in the stirred reactor using a series of organic compounds of successively higher boiling points to: 1) establish the boiling range where desorption occurred before reaction (thereby establishing the approximate threshold reaction temperature); and 2) provide an initial screening of the level destruction, and effect of process variables, for the higher boiling components where desorption is not important.

# 5.1.1 Test of Desorption versus Boiling Range

Several initial screening tests were done with topped crude oil mixed with soil to establish the temperature limits for desorption on heat up of the soil. The crude oil was used because it contained compounds with boiling points over a wide temperature range and provided a qualitative estimate of the temperature at which the reaction predominated over desorption. In these tests, GC scans of the recovered condensate, and extracts of the residual oil and the feed material, were compared for the carbon numbers of the n-paraffin peaks in each fraction. Running at 250°C, the transition from boiling range of the overhead to the residue (in a run without sulfur) corresponded closely to the reactor operating temperature (e.g.,  $n-C_{14}$ , BP 254°C). A comparison experiment in the presence of sulfur did

not show significant decrease in the boiling range of the overhead suggesting that these hydrocarbons did not react significantly below 250°C.

Next, a soil blend was prepared that was spiked with nine aromatic compounds (2000 ppm each, except pyrene at 1000 ppm) with boiling points from 165°C to 393°C mixed into the 75/25 SSM top soil blend. Several series of three sets of runs were carried out at 250°C, 350°C, and 440°C for 2 hours with 200 g soil and 30 g sulfur. Analysis of the recovered samples for the spiked organic compounds was compared with a sample of the original spiked soil. The results are presented in Table 4. Surrogate recoveries for all recovered fractions were in the 60 to 90% range.

In the experiment, a slow stream of nitrogen flowed through the reactor into an ice trap and then through a caustic scrubber before release to the hood. As described in Section 2.1.4, after the run, the reactor system is disassembled and three sample fractions, including equipment rinsings, are removed for analysis. These three product fractions are the raw reactor solids, the condensate in the ice trap, and any organic compounds extracted from the caustic scrubber. As expected, the ice trap condensate represents most of the desorbed material recovered.

The combined recovery from the three product fractions were compared with the analytical results from the extraction of the feed soil (based on a 200 g charge which nominally contains 400 mg of each compound except pyrene and 200 mg of pyrene) to arrive at a total recovery for each compound. This procedure corrects for losses in the experiment, sampling, and analysis. It should also be noted that absolute recoveries of mesitylene and durene in both the soil charge and product analyses were about 70% and below the values of 85 to 90% observed for the higher boiling compounds spiked in the soil. These compounds are technically not semivolatile organics (defined as BP > 200 °C) and are therefore outside the method range for the Soxhlet extraction (Method 3540) used for the sample work up and therefore recoveries were lower.

These tests measured the performance of two processes which are in competition: desorption and chemical destruction. The relative importance of these two processes vary with the boiling point of the constituent. The five lower boiling compounds show relative recoveries of about 85-90% for all three runs. Based on the relatively constant recovery factor observed for these compounds, it is concluded that these represent thermal desorption only with negligible effects of chemical destruction. The decreased total recoveries for the four higher boiling compounds show the effect of the competition of chemical destruction with desorption. Bibenzyl and hexachlorobenzene still yield significant recoveries in the overhead fractions with destruction representing about 20% of the total compound fed. As the boiling point is further increased, the fraction of feed compound that is destroyed increases markedly.

Table 4 shows three different measures of process performance: recovery from the overhead, destruction, and destruction and removal efficiency (DRE) of the treated soil. These measures are discussed further.

#### Table 4 Effect of Boiling Point on Destruction and Removal

4a. Reactor run at 250 C and 2 Hour Residence Time

| Compound          | RP  | Charge | Beactor  | Becovery in | Becovery in |        | Percent   | Parcent   | Destruction & |
|-------------------|-----|--------|----------|-------------|-------------|--------|-----------|-----------|---------------|
|                   | 51  | (mg)   | Residual | ice Trap    | Scrubber    | Total  | recovered | Destroyed | Efficiency    |
| mesitylene        | 165 | 276.9  | 0.15     | 225,5       | 0.35        | 226    | 81.6%     | 18.4%     | 99.9%         |
| durene            | 197 | 276.2  | 0.15     | 249.3       | 0.08        | 249.53 | 90.3%     | 9.7%      | 99.9%         |
| naphthalene       | 218 | 343.7  | 0.65     | 287.9       | 0.17        | 288.72 | 83.8%     | 16.0%     | 99.8%         |
| 2-Me Naphthalene  | 241 | 353    | 1.07     | 276.9       | 0.06        | 278.03 | 78.5%     | 21.2%     | 99.7%         |
| biphenyl          | 254 | 368.5  | 3.11     | 295.8       | 0.06        | 298.97 | 80.3%     | 18.9%     | 99.2%         |
| bibenzyl          | 285 | 356.8  | 3.87     | 229.2       | 0.00        | 233.07 | 64.2%     | 34.7%     | 98.9%         |
| hexachlorobenzene | 322 | 327.5  | 8.60     | 204.4       | 0.36        | 213.36 | 62.5%     | 34.9%     | 97.4%         |
| anthracene        | 340 | 306.1  | 7.32     | 64.0        | 0.00        | 71.32  | 20.9%     | 76.7%     | 97.6%         |
| pyrene            | 393 | 175    | 2.56     | 6,9         | 0,00        | 9,46   | 3.9%      | 94.6%     | 98.5%         |

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#### 4b Reactor Run at 350 C and 2 Hours Residence Time

| Compound          | BP  | Charge<br>(mg) | Reactor<br>Residual | Recovery in | Recovery in<br>Scrubber | Total  | Percent | Percent<br>Destroyed | Destruction &<br>Removal |
|-------------------|-----|----------------|---------------------|-------------|-------------------------|--------|---------|----------------------|--------------------------|
| mesitylene        | 16  | 5 276.9        | 1 13                | 220.3       | 2.98                    | 224 41 | 80.6%   | 19.0%                | 99.6%                    |
| durene            | 19  | 7 276.2        | 0.27                | 245.6       | 5.09                    | 250.96 | 90.8%   | 9.1%                 | 99.9%                    |
| naphthalene       | 21  | 343.7          | 0.2                 | 296.3       | 8.25                    | 304.75 | 88.6%   | 11.3%                | 99.9%                    |
| 2-Me Naphthalene  | 24  | I 353          | 0.15                | 281.8       | 7.24                    | 289.19 | 81,9%   | 18.1%                | >99.9%                   |
| biphenyl          | 254 | <b>1</b> 368.5 | 0.32                | 298,4       | 7,68                    | 306,4  | 83.1%   | 16.9%                | 99.9%                    |
| bibenzyl          | 28  | 5 356.8        | 0.28                | 221.5       | 4.67                    | 226.45 | 63,4%   | 36,5%                | 99.9%                    |
| hexachlorobenzene | 323 | 2 327.5        | 17.66               | 96,5        | 2.11                    | 116.27 | 30.1 %  | 64.5%                | 94.6%                    |
| anthracene        | 340 | 306.1          | 9.15                | 23.3        | 0.59                    | 33.04  | 7.8%    | 89.2%                | 97.0%                    |
| pyrene            | 39: | 3 175          | 2.71                | 2.3         | 0.04                    | 5.05   | 1.3%    | 97.1%                | 98.5%                    |

4c. Reactor run at 440 C and 2 Hour Residence Time

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|                   |     |        |          |             |             |        |           |           | Destruction & |
|-------------------|-----|--------|----------|-------------|-------------|--------|-----------|-----------|---------------|
| Compound          | BP  | Charge | Reactor  | Recovery in | Recovery in |        | Percent   | Percent   | Removal       |
|                   |     | (mg)   | Residual | Ice Trap    | Scrubber    | Total  | recovered | Destroyed | Efficiency    |
| mesitylene        | 165 | 276.9  | 0.27     | 243.8       | 4.24        | 248,31 | 89.6%     | 10.3%     | 99,9%         |
| durene            | 197 | 276.2  | 0.08     | 245.8       | 10.15       | 256.03 | 92.7%     | 7.3%      | >99.9%        |
| naphthalene       | 218 | 343.7  | 0.09     | 280.2       | 12.48       | 292.77 | 85.2%     | 14.8%     | >99.9%        |
| 2-Me Naphthalene  | 241 | 353    | 0.08     | 269.2       | 8.22        | 277.5  | 78.6%     | 21.4%     | >99.9%        |
| biphenyl          | 264 | 368.5  | 0.15     | 282.5       | 7.64        | 290.29 | 78.7%     | 21.2%     | > 99.9%       |
| bibenzyl          | 285 | 356.8  | 0.08     | 228,8       | 4.87        | 233,75 | 65.5%     | 34.5%     | >99.9%        |
| hexachlorobenzene | 322 | 327.5  | 0.49     | 205.4       | 3.56        | 209.45 | 63,8%     | 36.0%     | 99.9%         |
| anthracene        | 340 | 306.1  | 0.35     | 69.0        | 1.22        | 70.57  | 22.9%     | 76.9%     | 99.9%         |
| pyrene            | 393 | 175    | 0.67     | 12.7        | 0.14        | 13.51  | 7.3%      | 92.3%     | 99.6%         |

#### **Recovery from Overhead**

The percentage recovery from overhead is a measure of the amount of a compound which is desorbed from the soil rather than reacted. It is calculated as the ratio between the total amount of the compound recovered in the ice traps and scrubber to the amount originally present in the soil.

#### Destruction

The percentage destroyed is a measure of the effectiveness of the sulfur in the reactor. The percentage destroyed was calculated simply as the difference between the amount originally present in the soil and the amount recovered both in the overhead and soil fractions, divided by the amount originally present in the soil.

#### **Destruction and Removal Efficiency (DRE)**

The DRE is a measure of overall removal of each compound from the soil. The DRE is calculated by subtracting the ratio of the amount of residual compound left in the soil to the amount originally present from one. For the lower boiling point compounds, it reflects primarily the effect of desorption. For the higher boiling compounds, it reflects reaction efficiency.

The differences in the recovery between hexachlorobenzene and anthracene, which have similar boiling points, are attributed to the expected much slower reaction rate for hexachlorobenzene with sulfur due to lack of hydrogen. Other research in this laboratory on reaction of sulfur with various chlorohydrocarbons has suggested the thermodynamics for hexachlorobenzene reaction with sulfur would be much less favorable [10].

Reaction temperature is not seen to greatly affect the recoveries as the desorption step removes the compound from further opportunity to react in the simple batch reactor system. The residual content of the treated soil is nonetheless greatly reduced, corresponding to DRE values of better than 99% at the higher reaction temperatures.

These same observations are noted whether the reaction temperature is 250°C, 350°C, or 440°C. The reduction in amount remaining in the reactor at 440°C for the higher boiling compounds, e.g., pyrene, suggests that reaction temperatures above 350°C may be needed to obtain complete destruction of the non-volatilized compounds in the soil.

These results suggest reaction begins about 250°C, or slightly less (there may be a slight amount of destruction for methyl naphthalene and biphenyl). The lower temperature limit for reaction can not be determined without an additional experiment at a lower temperature, since the time for volatilization during the ramp up to 250°C is much shorter than the two hour reaction interval at 250°C. Thus, desorption can occur before there is opportunity for reaction to occur at the lowest possible reaction temperature.

As discussed in the QAPP, duplicate analyses of some of the analyses were performed. Results of these analyses are presented in Appendix B.

## 5.1.2 Effect of Process Parameters

Preliminary tests were made of other process variables in additional runs at 250°C. These tests used only the four higher boiling aromatics listed in Table 4. The results are given in Table A-1 in Appendix A. These runs evaluated reaction times of 0.5 and 1 hour as well as sulfur contents of 4.8 % and 9.1 % for comparison with the run in Table 4 (2 hours and 13% sulfur). It was found that decreasing reaction time had a greater effect than decreasing sulfur/feed ratio, as might be expected, by increasing the residual organics in the reactor solids and decreasing the quantity carried over. Reaction times less than 2 hours may require temperatures higher than 250°C.

## 5.2 VAPOR REACTOR

Results are presented for destruction of toluene in the vapor reactor in order to establish conversion efficiency as a function of process variables. From these results, a kinetic model is developed in order to predict process conditions necessary to achieve a satisfactory destruction efficiency.

#### 5.2.1 Test Results

Twelve experiments were conducted using the vapor reactor system. The major parameters varied included toluene inlet vapor concentrations, residence times, and operating temperatures. In addition, the height of the liquid sulfur in the system was varied (affecting primarily the residence time), as well as the type of sparging inside the reactor, which was found to have little overall effect on the reaction.

Several preliminary experiments were performed to shakedown the experimental equipment and procedures. During these preliminary experiments, only weight gain to the trap was measured and no gas chromatograph (GC) analyses were performed. Therefore, accurate outlet toluene concentrations were not obtained.

The data from experiments in which GC analyses were performed are presented in Table 5. The data in Table 5 is sorted by temperature, and gives the run number, residence time, inlet and outlet toluene concentrations in the overall feed stream in parts per million (molar ratio), and percentage toluene destroyed.

The inlet toluene concentrations were determined by finding the mass difference in the container of toluene feed before and after each run. This was converted to a molar amount and divided by the total moles of nitrogen fed to the system (calculated assuming the ideal gas law) to determine the toluene concentration. The outlet toluene concentrations were determined by GC analyses of the material found in the ice traps. Again, the toluene effluent was divided by the overall gas flow rate to determine concentration.

| Table 5. Vapor Reactor Results |          |                         |                           |                            |                                  |
|--------------------------------|----------|-------------------------|---------------------------|----------------------------|----------------------------------|
| Reactor<br>Temp(°C)            | Run<br># | Resid.<br>Time<br>(sec) | Inlet<br>Toluene<br>(ppm) | Outlet<br>Toluene<br>(ppm) | Destruction<br>Efficiency<br>(%) |
| 300                            | 8        | 149                     | 5847                      | 1494                       | 74                               |
| 300                            | 12       | 150                     | 8233                      | 3345                       | 41 ·                             |
| 300                            | 15       | 262                     | 4711                      | 1675                       | 64                               |
| 300                            | 17       | 543                     | 5648                      | 1303                       | 77                               |
| 350                            | 10       | 138                     | 9262                      | 5455                       | 41                               |
| 350                            | 11       | 138                     | 16983                     | 11488                      | 32                               |
| 350                            | 13       | 138                     | 8902                      | 4220                       | 53                               |
| 350                            | 14       | 118                     | 7719                      | 2676                       | 65                               |
| 350                            | 16       | 241                     | 4502                      | 1152                       | 74                               |
| 350                            | 18       | 500                     | 5105                      | 760                        | 85                               |
| 350                            | 19       | 667                     | 5217                      | 217                        | 96                               |
| 400                            | 20       | 216                     | 3449                      | 1943                       | 44                               |
| 400                            | 9        | 127                     | 7719                      | 2161                       | 72                               |

## 5.2.2 Model for Vapor Reactor System

It was anticipated that the vapor reactor would operate with first order kinetics, which would imply a zero-intercept linear relationship between the logarithm of the output/input concentration ratios and the residence time, as shown below:

 $\ln (C/C_0) = -kt$ 

C is the concentration of toluene in the vapor stream as a function of time, and  $C_o$  is the initial concentration of the toluene fed to the reactor, t is residence time (in seconds), and k is the rate constant.

The rate constant k is a function of temperature according to the Arrhenius relationship:

 $k = A \exp \left(-E_a/RT\right)$ 

in which A is a reaction constant, E<sub>a</sub> is the activation energy for the reaction (in cal/gmol), R is the universal gas constant, 1.987 cal/gmol-°K, and T is the reaction temperature (in °K).

Figure 4 graphically depicts the first order data which were used to determine the rate constants at each reactor temperature. The figures show the function  $\ln(C/C_0)$  plotted against residence time. Figures 4a and 4b show the data obtained




at 300 and 350°C, respectively. The data were fitted to a line, using a standard least-squares fit, with a zero-intercept. The data from run #8, which can be seen to be quite distant from the line in Figure 4a, was not used in the least-squares algorithm. This was the first run performed during the experiment, and the sulfur vapor reactor was inadvertently not purged prior to the test, which may have led to erroneous results. The rate constants calculated at 300 and 350°, were 0.0030/sec and 0.0046/sec, and the R-squared coefficients for the lines were 0.79 and 0.89, respectively. Because only two points were obtained at 400°C, a least-squares fit was impossible. However, k-values could be calculated for both runs, and these were averaged to obtain an overall k at 400°C of 0.0063/sec. This value was used to plot a line on Figure 4c, which falls approximately halfway between the two data points at that temperature.

The Arrhenius equation can be rearranged to yield a linear relationship between in k and the inverse of temperature:

 $\ln k = -E_a/R * 1/T + \ln A$ 

The natural logarithms of the k values obtained at the three reaction temperatures were plotted against the inverse of that temperature in Figure 5. The points were remarkably close to linear, and a least-squares fit yielded the following values:

 $\ln k = -2926/T - 0.71$ 

or,  $E_a = 5814$  cal/gmol and k = 0.49 exp (-2926/T), with T in °K and k in sec<sup>-1</sup>, which is the required result. The R-squared for this fit was 0.99, indicating that the three points are collinear as predicted. (The R-squared value was coincidentally higher than anticipated given the uncertainties in the data.) Figure 6 shows the empirical fit for the data, calculated versus actual destruction, with the calculated destruction determined using the Arrhenius relationship determined above.

#### 5.2.3 Residence Times and Reactor Sizes

Based on the first order model and extrapolations from data obtained at lower temperatures and destruction efficiencies, the residence time required for 99% destruction of toluene at the three tested reactor temperatures, and one additional higher temperature, were determined:

| Table 6. Calculated Residence Times |                      |  |  |  |  |  |
|-------------------------------------|----------------------|--|--|--|--|--|
| Temperature (°C)                    | Residence Time (sec) |  |  |  |  |  |
| 300                                 | 1535                 |  |  |  |  |  |
| 350                                 | 1010                 |  |  |  |  |  |
| 400                                 | 730                  |  |  |  |  |  |
| 500 (extrapolated)                  | 419                  |  |  |  |  |  |

These residence times were approximations only, but were calculated to determine the rough order of magnitude for the reactor volume and residence times. An approximate breakdown of the effluent gases can be predicted assuming a 10,000 kg/hour unit, which processes soil containing 10% (by weight) moisture and 0.5% by weight organics (MW = 100), 75% of which is converted in the soil and 25% of which are volatilized. If minimal nitrogen purge is assumed, the waste stream will consist of:





| Table 7. Vapor Stream |                 |  |  |  |  |  |  |
|-----------------------|-----------------|--|--|--|--|--|--|
| Constituent           | Molar Flow      |  |  |  |  |  |  |
| Water                 | 50 kg-moles/hr  |  |  |  |  |  |  |
| Hydrogen sulfide      | 3 kg-moles/hr   |  |  |  |  |  |  |
| Organics              | 0.2 kg-moles/hr |  |  |  |  |  |  |
| Nitrogen (purge)      | 6 kg-moles hr   |  |  |  |  |  |  |
| TOTAL                 | 60 kg-moles/hr  |  |  |  |  |  |  |

The vapor reactors will need to be sized to handle the above flow rates. The following table shows the required size of the vapor reactors containing the whole flow, or the flow without the water vapor (assuming it is condensed out of the stream), at various operating temperatures. These estimates are developed assuming that the gases are ideal, at one atmosphere pressure.

| Table 8. Calculated Vapor Reactor Volume |  |   |  |  |  |  |  |  |
|--|--|---|--|--|--|--|--|--|
| Temperature (°C)                         | Volume (m <sup>3</sup> ) assuming all gases in reactor | Volume (m <sup>3</sup> ) assuming<br>water is removed |  |  |  |  |  |  |
| 300                                      | 1200   | 200   |  |  |  |  |  |  |
| 350                                      | 860  | 170   |  |  |  |  |  |  |
| 400                                      | 670  | 135   |  |  |  |  |  |  |
| 500                                      | 440  | 90  |  |  |  |  |  |  |

The key result from this analysis was that the required reactor volumes are extremely large for transportable units, even assuming that the water vapor is removed. Obviously, the reactor volumes could be decreased by increasing the pressure at which the reaction is conducted, but then a pressure vessel, compressors, and other processing equipment would be required. This option would have to be economically and technically evaluated to find the optimal feasible pressure.

Based on these results, the vapor section (freeboard volume of the second section) of the rotary soil reactor (Section 2.4) was designed to provide a nominal vapor residence time of between three and five minutes. This would allow for destruction of organic compounds in the range of 40 to 85%, for temperatures of 300 to 400°C respectively, while not being too large as to be unwieldy for the test application.

#### 6.0 METALS STABILIZATION

In this section, processing tests of various metal-spiked soils are discussed to determine the specific heavy metals, the applicable concentration range, and the process conditions, for which the Sulchem Process will immobilize the metals.

#### 6.1 TESTS WITH DIFFERENT METALS

A series of batch screening runs were made on several soil blends containing various heavy metals. The purpose of these initial tests were to find how well each of the various heavy metals responded to the sulfur treatment of the Sulchem Process. A *priori* one might expect that the stabilization mechanism might be the formation of metal sulfides as an insoluble coating. If this is the case, then the heavy metals whose sulfides are soluble in acid (i.e., chromium, cobalt, iron, nickel, and zinc) might not be rendered immobile as much as other metals (e.g., lead) with the Sulchem treatment since the TCLP test leaches the sample with a buffered acetic acid solution. It was for the purpose of examining this premise that the initial metal screening tests were made.

More detail on the effect of process conditions on TCLP reduction are described in the next section. For the screening studies to compare the behavior of different heavy metals reported here, the process parameters were sulfur to soil ratio, reaction temperature, and reaction time. Generally one sulfur to soil ratio was used (typically 0.15), a range of reaction temperatures were used (e.g., 250°C, 300°C, and 350°C), and the reaction time was typically one-half hour.

The initial metal screening tests were done on soil samples of SARM-III, as well as prepared blends of metals spiked in either SSM soil or a 75/25 blend of SSM and horticultural topsoil. The SARM samples had been prepared with arsenic trioxide  $(As_2O_3)$ , cadmium sulfate  $(CdSO_4)$ , chromium nitrate  $(Cr(NO_3)_3)$ , copper sulfate  $(CuSO_4)$ , lead sulfate  $(PbSO_4)$ , nickel nitrate  $(Ni(NO_3)_2)$ , and zinc oxide (ZnO).

Screening studies of various metals were made with a series of closed mode reaction runs made on five separate metal/SSM mixtures. These individual blends were made using lead oxide (PbO), cadmium oxide (CdO), arsenic oxide  $(As_2O_3)$ , chromium (III) oxide  $(Cr_2O_3)$ , and nickel hydroxide  $(Ni(OH)_2)$  to contain 1000 ppm of each of the metals. TCLP analyses were made of the soil blend as well as the three raw reactor products from each processing temperature. Two hour reaction runs were used in these tests which were conducted in the closed mode unstirred reactor. These data are listed in Table 9. It was concluded that both lead and cadmium responded to the treatment, the latter more at elevated temperatures. For example, cadmium had a TCLP of 38.9 mg/L. This was reduced to 8.3 mg/L at the mildest conditions and at temperatures of 350°C reduced to below the regulatory limit of 1.0 mg/L. The results on the arsenic and nickel were inconclusive.

Next, SARM-III was run to evaluate the performance of the different contained heavy metals. These runs were carried out in the stirred reactor autoclave to ensure that adequate mixing was used. Since the objective was to determine metals stabilization, no analyses were made on these runs for the contained organic compounds also present in the SARM-III.

 Table 9. Tests of Various Metals vs. Reaction Temperature

| Temp<br><u>°C</u> | Time<br><u>Hrs</u> | Sol               | <u>S/soil</u>        | Pb<br>ppm            | PbTCLP<br>mg/L       | Cd<br>ppm               | CdTCLP<br><u>mg/L</u> | As<br>ppm            | As TCLP<br><u>mg/L</u> | Cr<br>ppm            | CrTCLP<br>mg/L          | Ni<br>ppm               | NiTCLP<br><u>mg/L</u> |
|-------------------|--------------------|-------------------|----------------------|----------------------|----------------------|-------------------------|-----------------------|----------------------|------------------------|----------------------|-------------------------|-------------------------|-----------------------|
|                   | Unt                | reated blend      | d                    | 1000                 | 14.4                 | 1000                    | 38.9                  | 1000                 | 3.07                   | 1000                 | < 0.05                  | 1000                    | 1.51                  |
| 250<br>300<br>350 | 2<br>2<br>2        | SSM<br>SSM<br>SSM | 0.25<br>0.25<br>0.25 | 1000<br>1000<br>1000 | 0.69<br>0.58<br>0.20 | 1 000<br>1 000<br>1 000 | 8.34<br>4.43<br>0.62  | 1000<br>1000<br>1000 | 5.97<br>8.23<br>11.7   | 1000<br>1000<br>1000 | <0.05<br><0.05<br><0.05 | 1 000<br>1 000<br>1 000 | 0.89<br>1.21<br>1.16  |

Table 10 shows the results for the SARM-III feed. For the main metals present in the SARM-III TCLP leachate (i.e., all but arsenic and chromium), copper responds the most effectively to the Sulchem Process decreasing the TCLP value 100-fold at the mildest conditions and to the detection limit at the highest temperature, presumably because of insoluble sulfide formation. In Table 10 a continuous reduction of TCLP nickel leachate levels for the treated soils is shown at successively higher temperatures, from 22.2 mg/L to 17.3 mg/L at 250°C to 0.4 mg/L at 440°C. The results for cadmium, lead, and zinc also demonstrate some temperature effect, but not as extensive as observed for nickel.

Based on these results, additional test blends were prepared using the oxides or hydroxides of lead, cadmium, nickel, and zinc to further evaluate the process conditions necessary to improve the TCLP results on the treated soils for these four metals. It was felt important to evaluate the stabilization of these metals in soils with a higher organic carbon content than those employed above. Therefore, the next series of tests was based on using the 75/25 SSM top soil blend, which was used in all of the subsequent tests. These experiments were all run in the stirred reactor.

The first four data sets in Table 11 shows runs on various blends of Cd, Pb, Ni, and Zn as a function of temperature. The first three test blends were at relatively high loading of metals to evaluate possible process limits for reduction of the leachate to TCLP limits. The cadmium results demonstrate the previously observed effect of process temperature on the reduction of TCLP, although the effect of process temperature is much less for lead in this case. Substituting the more soluble nitrate at the same lead loading demonstrates how the more soluble form can prevent reaching the TCLP regulatory limit of 5 mg/L in this case. Although somewhat higher TCLP levels are observed for the starting soil blend using more soluble salts, the response of the soil to the Sulchem treatment shows comparable reduction in TCLP values. The nickel and zinc spiked SSM topsoil blend did not demonstrate as great an effect of process temperature effect previously noted for these metals in the SARM blend (Table 10).

Based on the results from these three tests with high levels of added metals in 75/25 SSM/soil blend, as well as the results from the SARM-III tests (Table 10), a fourth blend was prepared at intermediate concentrations of Cd, Pb, Ni, and Zn and run at various temperatures. This blend was prepared in order to more fully challenge the process at the highest concentrations possible and yet still achieve a passing TCLP for the treated soils.

The results for the fourth blend in Table 11 however turned out to not adequately challenge the process for all of the metals. These experiments demonstrate significant reduction of TCLP values for the treated soils for lead and, at elevated temperatures, for cadmium. Zinc was not greatly reduced and the nickel results were inconclusive due to too low a TCLP value for the starting soil. Tests of additional blends with higher metal contents are needed to arrive at a more suitable demonstration test mixture.

Finally in Table 11, a soil blend was then spiked to 10,000 ppm by weight of cobaltous (II) oxide and run at several temperatures. In contrast with the other metals, lower treatment temperatures actually *enhance* the leachability of the cobalt from the added cobaltous oxide. This may be due to formation of a more acid soluble surface on the particles.

# Table 10.Test of SARM III Soil vs. Reaction Temperature

|                                  | Untreated   | Soil  | <u> </u>  | Re  | eaction Prod   | lucts   | <u>,</u>   |
|----------------------------------|---|---|---|---|--|---|--|
| Run No.                          |   |   | 27-77   | 27-78   | 27-79  | 27-84   | 27-92  |
| Temp °C                          |   |   | 250   | 300   | 350  | 400   | 440  |
| Time hr                          |   |   | 0.5   | 0.5   | 0.5  | 0.5   | 0.5  |
| Sulfur %                         |   |   | 13.0%   | 13.0%   | 13.0%  | 13.0%   | 13.0%  |
| <u>Metal</u>                     | Contained<br>Metal<br><u>mg/kg</u>                          | TCLP<br>mg/L  | TCLP<br>mg/L  | TCLP<br>mg/L  | TCLP<br>mg/L   | TCLP<br>mg/L  | TCLP<br><u>mg/L</u>                                    |
| As<br>Cd<br>Pb<br>Ni<br>Cu<br>Zn | 500<br>1,000<br>1,500<br>14,000<br>1,000<br>9,500<br>22,500 | 0.21<br>36.8<br><0.05<br>35.5<br>22.2<br>153<br>791 | 0.16<br>22.5<br>0.07<br>25.5<br>17.3<br>1.13<br>628 | 0.23<br>15.1<br>0.12<br>22.7<br>6.71<br>0.05<br>361 | 0.37<br>12.4<br><0.05<br>21.2<br>3.72<br>0.03<br>162 | 0.21<br>6.02<br><0.05<br>16.1<br>0.72<br>0.03<br>58.1 | <0.05<br>3.66<br><0.05<br>12.2<br>0.4<br><0.01<br>32.4 |

|                     |                   | Untreated       | Soil         |               | R            | eaction Proc   | lucts        |              |
|---------------------|-------------------|-----------------|--------------|---------------|--------------|----------------|--------------|--------------|
| Run No.<br>Temp °C  |                   |                 |              | 27-69<br>250  | 27-71<br>300 | 27 - 70<br>350 | 27-76<br>400 | 27-91<br>440 |
| Time hr             |                   |                 |              | 0.5           | 0.5          | 0.5            | 0.5          | 0.5          |
| Sulfur %            |                   |                 |              | 13.0%         | 13.0%        | 13.0%          | 13.0%        | 13.0%        |
|                     |                   | Contained       |              |               |              |                |              |              |
|                     |                   | Metal           | TCLP         | TCLP          | TCLP         | TCLP           | TCLP         | TCLP         |
| Metal               | <u>Salt added</u> | <u>mg/kg</u>    | <u>mg/L</u>  | <u>mg/L</u>   | <u>mg/L</u>  | <u>mg/L</u>    | <u>mg/L</u>  | mg/L         |
| Cd                  | CdO               | 5,000           | 144          | 28.3          | 42.0         | 22.4           | 4.41         | 0.54         |
| Pb                  | РЬО               | 10,000          | 61.7         | 4.08          | 1.22         | 1.21           | 2.21         | 2.03         |
| Run No.             |                   |                 |              | 33-40         |              |                |              | 33-41        |
| Temp °C             |                   |                 |              | 250           |              |                |              | 440          |
| Timehr<br>Sultur≪   |                   |                 |              | 0.5<br>13.0%  |              |                |              | 0.5          |
|                     |                   |                 |              | 10.076        |              |                |              | 10.0%        |
|                     |                   | Contained       |              | 7010          |              |                |              |              |
| Matal               | Soltadad          | Metal<br>ma (ka | TCLP         |               |              |                |              | TCLP         |
| wetar               | Saladded          | <u>mg/kg</u>    | <u>mg/c</u>  | <u>mg/c</u>   |              |                |              | <u>mg/L</u>  |
| Cd                  | CdCl2             | 1,000           | 30.1         | 4.98          |              |                |              | 0.31         |
| Pb                  | Pb(NO3)2          | 10,000          | 96.4         | 29.2          |              |                |              | 7.61         |
| Run No.             |                   |                 |              | 27-95         | 2796         | 27-97          |              |              |
| Temp °C             |                   |                 |              | 250           | 300          | 350            |              |              |
| Time hr             |                   |                 |              | 0.5           | 0.5          | 0.5            |              |              |
| Sulfur %            |                   |                 |              | 13.0%         | 13.0%        | 13.0%          |              |              |
|                     |                   | Contained       |              |               |              |                |              |              |
| <b>NF</b> . 4 . 1   | 0-14              | Metal           | TCLP         | TCLP          | TCLP         | TCLP           |              |              |
| Metal               | Satadded          | mg/kg           | <u>mg/L</u>  | <u>mg/L</u>   | <u>mg/L</u>  | <u>mg/L</u>    |              |              |
| Ni                  | Ni(OH)2           | 2,000           | 0.54         | 1.95          | 2.5          | 4.7            |              |              |
| Zn                  | ZnO               | 2,000           | 36.3         | 25.6          | 22.60        | 24.80          |              |              |
| Run No.             |                   |                 |              | 33-12         | 33-13        | 33-14          | 33-15        |              |
| Temp °C             |                   |                 |              | 250           | 300          | 350            | 400          |              |
| Time hr<br>Sulfur % |                   |                 |              | 0.5           | 0.5          | 0.5            | 0.5          |              |
| Guildt 76           |                   |                 |              | 10.070        | 10.075       | 10.074         | 10.078       |              |
|                     | *                 | Contained       | TOUR         |               | TOLD         |                |              |              |
| Metal               | Salt added        | ma/ka           | ma/l         | ma/l          | ma/l         | ma/l           | ma/l         |              |
| wora                |                   | <u>119/119</u>  | <u>109/6</u> | <u>1119/2</u> | <u></u>      | <u></u>        | mg/L         |              |
| Cd                  | CdO               | 200             | 2.37         | 0.33          | 0.17         | < 0.01         | < 0.01       |              |
| Pb                  |                   | 2,000           | 2.40         | 0.38          | 0.41         | <0.10          | <0.10        |              |
| Zn                  | ZnO               | 500             | 6.76         | 3.49          | 4.60         | 0.80           | 0.11         |              |
| Due Ma              |                   |                 |              |               |              | 02 40          |              |              |
| Temp °C             |                   |                 |              |               |              | 350            |              | 23-42        |
| Time hr             |                   |                 |              |               |              | 0.5            |              | 0.5          |
| Sulfur %            |                   |                 |              |               |              | 13.0%          |              | 13.0%        |
|                     |                   | Contained       |              |               |              |                |              |              |
|                     |                   | Metal           | TCLP         |               |              | TCLP           |              | TCLP         |
| <u>Metal</u>        | Salt added        | <u>mg/kg</u>    | <u>mg/L</u>  |               |              | <u>mg/L</u>    |              | mg/L         |
| Co                  | CoO               | 10,000          | 15.0         |               |              | 65.8           |              | 11.3         |

## Table 11. Cd, Pb, Ni, Zn, and Co vs. Reaction Temperature 75/25 SSM/Top Soil Blend

#### 6.2 TESTS OF PROCESS PARAMETERS

The tests reported in the previous section include some process parameter comparisons at different reaction temperatures. Additional process parameters which were also studied included reaction time, process stoichiometry (sulfur to soil ratio), and metal content. Based on the results of the metal screening runs above, it was decided to concentrate these process tests for lead and cadmium in the 75/25 SSM topsoil blend. A number of these test results are presented in Table 12 along with several runs on a field sample containing lead. All experiments were run in the stirred autoclave reactor.

#### 6.2.1 Stoichiometry

The effect of reaction stoichiometry, as indicated by sulfur content of the feed, was evaluated. From the data set in Table 12 all run at the same temperature and reaction time (250°C and 0.5 hr), Figures 7 and 8 present a plot of the TCLP of the treated soils for lead and cadmium as a function of sulfur content of the reactor feed. A clear asymptotic dependence is noted as a function of sulfur content of the reactor feed. The curves are based on a fit of TCLP results to inverse sulfur content. The main point is that the asymptotic TCLP value is finite. That is, increasing sulfur content beyond some point does not further reduce the TCLP value of the treated soil. A sulfur content in the range of 15 to 20 percent apparently is sufficient to reduce the TCLP of the treated soil as far as it will go.

The asymptotic TCLP value at higher sulfur contents however varies with the heavy metal and the metal content. Thus for the more concentrated blend tested in Table 12, a passing TCLP for cadmium (< 1 mg/L) on the treated soil could not be achieved, at these processing conditions, whereas lead could be made to pass (< 5 mg/L) with sufficient sulfur addition.

#### 6.2.2 Temperature

Elevated temperatures further reduce the TCLP value somewhat although the temperature effect for cadmium and nickel as an example (Tables 10, 11, and 12) is greater for temperatures near the boiling point of sulfur (445 °C) whereas the temperature effect is much less pronounced for lead.

#### 6.2.3 Reaction Time

A limited number of runs were made at longer reaction times (see Table 12). Some further reduction in the TCLP of the treated soil was observed on these runs, but the level of reduction achievable is not as great as that observed by increasing the temperature or the sulfur/soil stoichiometry.

#### 6.3 OTHER TESTS

In this section several sets of experiments are described, which were performed to evaluate additional process approaches or modifications for consideration.

| Run           | Temp        | Time       | S/soil | – Soil I | Mixture –       | Pb    | Pb TCLP     | Cd   | Cd TCLP     |
|---------------|-------------|------------|--------|----------|-----------------|-------|-------------|------|-------------|
| <u>NB 027</u> | <u>°C</u>   | <u>hrs</u> | •      | SSM      | <u>Top Soil</u> | ppm   | <u>mg/L</u> | ppm  | <u>mg/L</u> |
| 42            | Untreated   |            | 0      | 75       | 25              | 1000  | 0.79        |      |             |
| 44            | 250         | 2          | 0.05   | 75       | 25              | 1000  | 0.24        |      |             |
| 43            | 250         | 2          | 0.1    | 75       | 25              | 1000  | 0.22        |      |             |
| 52            | 250         | 2          | 0.15   | 75       | 25              | 1000  | 0.14        |      |             |
| 46            | 250         | 2          | 0.1    | 75       | 25              | 3000  | 0.34        |      |             |
| 47            | 250         | 2          | 0.1    | 75       | 25              | 5000  | 0.47        |      |             |
|               | Untreated   |            | 0      | Pe       | edricktown S    | oil   | 512.0       |      |             |
| 58            | 250         | 2          | 0.10   | Pe       | edricktown Se   | oil   | 77.1        |      |             |
| 56            | 250         | 2          | 0.25   | Pe       | edricktown S    | oil   | 82.4        |      |             |
| 67            | 250         | 2          | 1.00   | Pe       | edricktown S    | oil   | 30.3        |      |             |
| 57            | 350         | 2          | 0.25   | Pe       | edricktown S    | oil   | 78.5        |      |             |
| 53            | Untre ate d |            | 0      | 75       | 25              |       |             | 1000 | 13.8        |
| 55            | 250         | 2          | 0.05   | 75       | 25              |       |             | 1000 | 5.46        |
| 54            | 250         | 2          | 0.1    | 75       | 25              |       |             | 1000 | 4.37        |
| 63            | Untre ate d |            | 0      | 75       | 25              | 10000 | 61.7        | 5000 | 144         |
| 66            | 250         | 0.5        | 0.05   | 75       | 25              | 10000 | 7.53        | 5000 | 88.6        |
| 65            | 250         | 0.5        | 0.10   | 75       | 25              | 10000 | 5.95        | 5000 | 70.3        |
| 69            | 250         | 0.5        | 0.15   | 75       | 25              | 10000 | 5.46        | 5000 | 28.3        |
| 64            | 250         | 0.5        | 0.25   | 75       | 25              | 10000 | 3.39        | 5000 | 33.8        |
| 72            | 250         | 0.5        | 0.50   | 75       | 25              | 10000 | 3.36        | 5000 | 28.9        |
| 73            | 250         | 0.5        | 1.00   | 75       | 25              | 10000 | 4.88        | 5000 | 24.5        |
| 71            | 300         | 0.5        | 0.15   | 75       | 25              | 10000 | 1.22        | 5000 | 42.0        |
| 70            | 350         | 0.5        | 0.15   | 75       | 25              | 10000 | 1.21        | 5000 | 22.4        |
| 76            | 400         | 0.5        | 0.15   | 75       | 25              | 10000 | 2.21        | 5000 | 4.4         |
| 74            | 250         | 1.0        | 0.15   | 75       | 25              | 10000 | 2.84        | 5000 | 38.3        |
| 75            | 250         | 2.0        | 0.15   | 75       | 25              | 10000 | 1.24        | 5000 | 27.5        |

## Table 12. Results of Process Parameter Tests – Pb and Cd







#### 6.3.1 Two Stage Runs

The reaction time process parameter discussed above for these small batch experiments is not well defined due to heat up and cool down times contributing to the total reaction time interval. Evidence for some further reduction in the TCLP of the metals in the treated soils as a function of run time suggests additional reaction time will enhance the TCLP reduction. Experiments were done to examine successive batch treatment in which the product from the first run was used as feed for the second run.

The runs were carried out at 250°C, 0.5 hour, and S/soil ratio of 0.15 (i.e., total sulfur content 13.0 percent). Two duplicate runs were made at these conditions to prepare enough material, after sampling for analysis of the first stage product, to feed to the second stage. An <u>additional</u> 13 percent of fresh sulfur was added for the second stage run. Thus, in comparing the results from the second stage run, one needs to consider the added reaction time, the additional dilution of the metal and the additional sulfur used.

The results are displayed in Table 13 along with comparable runs with longer run times and higher sulfur loading. The contained metal content of the reactor feed includes the dilution of the added sulfur. The percent leached by the TCLP test of the raw reactor product (based on 100 g of soil in 2 liters of leachate) is also displayed as well the metal concentration in the final leachate.

There are, however, no comparable runs with <u>both</u> added reaction time and higher sulfur loading, but the results for both lead and cadmium seem consistent with the earlier single stage tests (Table 12) if both reaction time and sulfur loading are considered. Thus, where further processing is justified, added stages of processing may accomplish it by extending the reaction time.

#### 6.3.2 Soluble Sulfides

It is well known that addition of soluble sulfide in water-based solidification/ stabilization media are able to decrease TCLP leachate values for contained heavy metals by precipitation or formation of a layer of insoluble metal sulfide. In the Sulchem Process, excess elemental sulfur is heated up with the soil and presumed to also react to form insoluble sulfides. This will occur however only if there is a reducing agent present to reduce the elemental sulfur to sulfide ion. Thus, even with the large excess of sulfur, there may still not be sufficient soluble sulfide present to fully convert the metals to an insoluble sulfide form.

Accordingly, several screening tests were carried out on different heavy metal spiked soils with sodium sulfide nonahydrate added to the reaction mixture. Table 14 summarizes the comparison runs at both 250°C and 440°C for the different metal spiked soils with added sodium sulfide compared with runs (reported above) at similar reaction conditions without the added soluble sulfide.

A striking reduction in the TCLP values with added sulfide are noted. Extending the reaction temperature to 440 °C and adding a soluble sulfide to the process reagents provides a passing TCLP of the treated soil for metals such as cadmium, nickel, cobalt and zinc. The results with lead are mixed.

## Table 13. Two Stage Run

|   | · .        |                    |            |        |                     |                              | Lead                      |         | С                            | admium                    |         |
|---|------------|--------------------|------------|--------|---------------------|------------------------------|---------------------------|---------|------------------------------|---------------------------|---------|
| Run                                       | Temp<br>°C | Time<br><u>hrs</u> | Soil<br>_g | Sulfur | S<br><u>Content</u> | Reactor<br>feed<br>Pb<br>ppm | TCLP<br>Pb<br><u>mg/L</u> | Leached | Reactor<br>feed<br>Cd<br>ppm | TCLP<br>Cd<br><u>mg/L</u> | Leached |
| First Stage<br>81,82                      | 250        | 0.5                | 200        | 30     | 13.0%               | 8696                         | 4.08                      | 0.94%   | 4348                         | 45.6                      | 20.98%  |
| Second Stage<br>83<br>Total reaction time | 250        | 0.5<br>1.0         | 178.2      | 51.8   | 22.5%               | 7748                         | 1.56                      | 0.40%   | 3874                         | 25.4                      | 13.11%  |
| Comparison Runs<br>64                     | 250        | 0.5                | 200        | 50     | 20.0%               | 8000                         | 3.39                      | 0.85%   | 4000                         | 33.8                      | 16.90%  |
| 74  | 250        | 1.0                | 200        | 30     | 13.0%               | 8696                         | 2.84                      | 0.65%   | 4348                         | 38.3                      | 17.62%  |

|  | Untreated   | Soi  | Run Without<br>Sulfide                       | Run With<br>Sulfide                      | Run Without<br>Sulfide                         | Run With<br>Sulfide                           |
|--|---|--|--|--|--|---|
|  | 75/25 SSM/soil -                                  | + Cd/Pb                                      |  |  |  |   |
| Run No.<br>Temp °C<br>Time hr<br>Sulfur %<br>Sulfide % | 10/20 0011/001                                    |  | 27-69<br>250<br>0.5<br>13.0%<br>0.0%         | 27 80<br>250<br>0.5<br>12.8%<br>2.1%     |  |   |
|  | Contained   |  |  |  |  |   |
| <u>Metal</u>   | Metal<br><u>mg/kg</u>                             | TCLP<br><u>mg/L</u>                          | TCLP<br>mg/L                                 | TCLP<br>mg/L                             |  |   |
| Cd<br>Pb   | 5,000<br>10,000                                   | 144<br>61.7                                  | 28.3<br>4.08                                 | 0.56<br>0.19                             |  |   |
| <u></u>  | SARM II   | 1  |  |  |  |   |
| Run No.<br>Temp °C<br>Time hr<br>Sulfur %<br>Sulfide % |   |  | 27 – 77<br>250<br>0.5<br>13.0%<br>0.0%       | 27-94<br>250<br>0.5<br>12.8%<br>2.1%     | 27 – 92<br>440<br>0.5<br>13.0%<br>0.0%         | 33 19<br>440<br>0.5<br>12.8%<br>2.1%          |
|  | Contained   |  |  |  |  |   |
| Metal  | Metal<br><u>mg/kg</u>                             | TCLP<br><u>mg/L</u>                          | TCLP<br>mg/L                                 | TCLP<br><u>mg/L</u>                      | TCLP<br><u>mg/L</u>                            | TCLF<br><u>mg/L</u>                           |
| As<br>Cd<br>Cr<br>Pb<br>Ni<br>Cu                       | 500<br>1,000<br>1,500<br>14,000<br>1,000<br>9,500 | 0.21<br>36.8<br><0.05<br>35.5<br>22.2<br>153 | 0.16<br>22.5<br>0.07<br>25.5<br>17.3<br>1.13 | 0.24<br>7.9<br>0.2<br>43.3<br>12<br>0.01 | <0.05<br>3.66<br><0.05<br>12.2<br>0.4<br><0.01 | 0.33<br>0.52<br><0.05<br>7.75<br>0.54<br>0.08 |
| Zn   | 22,500  | 791  | 628  | 482                                      | 32.4   | 9,93  |
|  | 75/25 SSM/soil -                                  | + Ni/Zn                                      |  |  |  |   |
| Run No.<br>Temp °C<br>Time hr<br>Sulfur %<br>Sulfide % |   |  | 27 - 95<br>250<br>0.5<br>13.0%<br>0.0%       | 27 – 98<br>250<br>0.5<br>12.8%<br>2.1%   | NA   | 3320<br>440<br>0.5<br>12.8%<br>2.1%           |
|  | Contained   |  |  |  |  |   |
| Metal  | Metal<br>* <u>mg/kg</u>                           | TCLP<br>mg/L                                 | TCLP<br>mg/L                                 | TCLP<br>mg/L                             |  | TCLP<br><u>mg/L</u>                           |
| Ni<br>Zn   | 2,000<br>2,000                                    | 0.54<br>36.3                                 | 1.95<br>25.6                                 | 0.72<br>6.79                             |  | <0.01<br>0.02                                 |
| <u></u>  | 75/25 SSM/soil -                                  | + Co   | ·  | ·····                                    |  |   |
| Run No.<br>Temp °C<br>Time hr                          |   |  |  |  | 23-42<br>440<br>0.5                            | 23-43<br>440<br>0.5                           |
| Sulfur %<br>Sulfide %                                  |   |  |  |  | 13.0%<br>0.0%                                  | 12.8%   |
| Sulfur %<br>Sulfide %                                  | Contained<br>Metal<br><u>mg/kg</u>                | TCLP<br>mg/L                                 |  |  | 13.0%<br>0.0%<br>TCLP<br><u>mg/L</u>           | 12.8%<br>2.1%<br>TCLP<br><u>mg/L</u>          |

### Table 14. Effect of Soluble Sulfide

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#### 6.3.3 Mineralogical Speciation

The original work plan expected to obtain mineralogical speciation of selected samples of processed treated soils in order to identify the chemical mineralogical mechanism for heavy metal stabilization using the Sulchem Process. No specific tests were done as part of this project, since a parallel effort on a separate project had evaluated the product from similar batch tests in the unstirred vented mode reactor of the SSM top soil blend to which salts of cadmium, mercury, and zinc were added. Standard optical microscopy, X-ray diffraction, and scanning electron microscope analyses were employed. These results are reported here to provide mineralogical information on a typical product.

The main mineralogical form found in the raw reactor product from this test was a slag-like material which was identified as a sulfur-rich cement. The heavy metals were found as sulfides as well as a complex cementing matrix of elemental sulfur, calcium oxides, and soil products. The predominant heavy metal phases present were: mercury-cadmium-sulfides with traces of zinc; zinc sulfide with traces of mercury, cadmium, and iron; and trace amounts of mercury and zinc associated with sulfur bearing soil silicate minerals. The heavy metal sulfides exhibit a wide range of particle sizes with the majority as fine particles in the 5 to 30 micron range.

#### 6.4 SUMMARY OF METALS TESTS

Preliminary results of the screening tests on different spiked soil mixtures provides the opportunity to assess the response of the different heavy metals to stabilization by the Sulchem Process. Each metal responds differently, but in general there will be a maximum metal content which can be processed to achieve passing TCLP leachate values. The precise maximum metal content which can be processed to passing TCLP values will vary somewhat based on the reaction temperature, reaction time, sulfur stoichiometry, or organic content of the soil. In general, however, a batch screening test at 250°C, sulfur content of the order of 10 to 15 percent and reaction time of 1/2 hour will define an approximate upper limit of the content of each metal which can be processed. Higher levels of metals can be processed to give passing TCLP by increasing the temperature and/or adding soluble sulfide, particularly for cadmium, nicked cobalt, and zinc. Increasing the stoichiometry or reaction time provides only a marginal improvement.

Recognizing that actual soil composition will affect the results, treatability studies are required to more precisely define the metal concentration envelope, which can be processed for a particular soil to give acceptable TCLP leachate values. Based on the very limited tests to date, lead limits of approximately 10,000 ppm and cadmium of several thousand ppm would seem to be generally feasible. Copper responds very well and nickel and zinc appear to be processed as well although the results are mixed. No definitive information on arsenic or chromium could be developed from the SARM-III tests.

#### 7.0 ROTARY SOIL REACTOR TESTS

CHMR conducted six tests for organic compound destruction using the rotary soil reactor described in Section 2.4. These tests were conducted using manufactured gas plant (MGP) site soils described in Section 3.3. The objectives of the tests were to demonstrate organic destruction at a larger scale using real Superfund soil and the Sulchem configuration present in the rotary reactor, and to determine the appropriate process conditions for optimal destruction. As designed, the rotary reactor was intended to present two sections to destroy the organic compounds: a soils reactor in which soil and sulfur are heated under inert atmospheres, and a vapor reactor in which the unreacted organic vapors desorbed in the first reactor are to react with molten sulfur.

Tests were not conducted using heavy metal contamination, because the MGP site soils did not contain appreciable quantities of heavy metal contamination, and because the stabilization of metals had been adequately demonstrated in previous experiments on a smaller scale.

#### 7.1 DESCRIPTION OF REACTIONS

Table 15 summarizes the reaction parameters and the results of the experiments. Runs were made at 300° and 350°C at reaction times of 0.5 and 1.0 hours. CHMR initially planned to conduct runs at temperatures below 300°C, but the results of initial runs indicated that the DRE would be too low at such temperatures. A one hour residence time at reaction temperature was used initially because it was thought to provide sufficient time for the reaction to proceed completely. A half hour residence time was used for two of the six runs to determine whether a half hour was sufficient for the reaction to proceed.

The sulfur/soil ratio was generally 10%, but runs were also conducted at 6 and 20%. Four of the runs were conducted with the soil as it was obtained from the site. Before conducting two of the runs, the soil was dried to reduce the moisture content and thereby reducing the vapor flow rate.

#### 7.2 RESULTS

Analyses were conducted using EPA Methods 3550, 3660, and 8100 which involve extraction with methylene chloride followed by analysis using gas chromatographic methods. The GC/FID results were quantitated by calibrating for four major constituents (2-methyl naphthalene, acenaphthene, phenanthrene, and pyrene) which covered the boiling point range for the contaminants in the soil. In addition to quantifying the recovery of these compounds, semi-quantitative recoveries for other constituents in the GC (which had been identified by GC/MS) could also be determined from the ratio of GC/FID peak areas for both the starting soil and the product fractions based on their relative quantities and dilutions as were done for the four compounds that were quantitated. These other constituents showed similar behavior of recovery as a function of boiling point.

#### 7.2.1 Overall GC Results

Figure 9 shows three typical chromatograms -- one from the untreated soil, the second from the condensate trap, and the third from the treated soil. The figure shows qualitatively how the products are separated between the reactor and the

## TABLE 15. SUMMARY OF ROTARY REACTOR TESTS

| RUN CONDITIONS<br>Run Number<br>Temperature, °C<br>Time, hrs  |  | Feed Soil                                 | 46-6<br>350<br>1  | 46-10<br>350<br>1                                  | 46-14<br>300<br>1                                  | 46-18<br>350<br>1                                      | 46-22<br>300<br>0.5                                       | 46-26<br>350<br>0.5  |
|---|--|---|---|--|--|--|---|--|
| CHARGE<br>Weight soil charged, g<br>Moisture content<br>Soil charged, mf, g<br>Sulfur charged, g<br>Percent Sulfur, mf, %                             |  | 20.1%                                     | 3688<br>20.1%<br>2946.7<br>220<br>6.9%                  | 2000<br>20.1%<br>1598.0<br>400<br>20.0%            | 2000<br>20.1%<br>1598.0<br>200<br>11.1%            | 1607<br>0.0%<br>1607.0<br>160<br>9.1%                  | 2000<br>13.5%<br>1730.6<br>200<br>10.4%                   | 2000<br>20.1%<br>1598.0<br>200<br>11.1%                    |
| PRODUCTS<br>Weight treated soil, g<br>First trap, g<br>Second trap, g<br>Caustic trap, g<br>Sulfur content<br>calculated H2S, g<br>weight increase, g | ţ  |   | 2742<br>581.4<br>69.8<br>3309.5<br>15.2%<br>532.8<br>NA | 1366<br>1429.6<br>2.6<br>4662.2<br>NA<br><br>172.9 | 2079.7<br>373.0<br>3.3<br>4546.8<br>NA<br><br>70.8 | 1670<br>27.7<br>1.9<br>4177.4<br>3.6%<br>159.8<br>86.7 | 1632.2<br>282.4<br>2.4<br>4537.4<br>2.8%<br>135.0<br>68.4 | 1632.0<br>349.1<br>5.4<br>4268.6<br>3.5%<br>158.7<br>151.4 |
| ORGANICS (mg/kg mf soil)<br>2-methyl naphthalene<br>acenaphthene<br>phenanthrene<br>pyrene<br>chrysene<br>benzopyrene/benzofluoranthene               | BP °C<br>241<br>278<br>340<br>393<br>448<br>>450 | 59<br>258<br>380<br>634<br>323 *<br>680 * | 55.96<br>20.61<br>51.48<br>3.98<br><0.05<br><0.05       | 25.26<br>9.84<br>13.88<br>0.08<br><0.05<br><0.05   | 72.12<br>22.50<br>63.94<br>0.58<br><0.05<br><0.05  | 20.69<br>12.76<br>58.08<br>1.99<br><0.05<br><0.05      | 118.38<br><0.05<br>62.97<br><0.05<br><0.05<br><0.05       | 109.87<br>17.07<br>173.94<br>7.08<br><0.05<br><0.05        |

NA = Not available or not determined

\* = GC/MS analysis



condensate. The scales of each have been adjusted so that the peak heights are approximately proportional to the amount of material present. (The scales are not identical since each extraction involved different sample size and dilution factor.) In the initial soil chromatogram, the retention time for the compounds are shown to range between 16 and 55 minutes, with the bulk of the compounds lying between 19 and 48 minutes. In the treated soil chromatogram, the relative proportion of most of the compounds is significantly diminished. Also, virtually all of the higher boiling compounds (with elution times greater than 35 minutes) have been eliminated. (The product fractions show contamination from the high temperature grease used in the rotating unions giving rise to a series of n-paraffin peaks ( $C_{22}$ - $C_{30}$ ), an antioxidant (methylene-bis ethyl, t-butyl phenol), and sitosterol which were identified by GC/MS. These are not considered in the analysis.) In the chromatogram of the condensate trap, no higher boiling point compounds are found above pyrene. However, significant quantities of lower boiling point compounds, which evidently desorbed from the soil, were present in the trap.

#### 7.2.2 Quantitative Results

Table 16 shows the run conditions and quantitative results from the experimental runs including individual product fractions. Several of the caustic traps were also extracted for organics, but very low quantities were found. Therefore the summary table only lists the reactor solids, condensate trap (trap #1), and the ice trap (trap #2). The percent recovered from the overhead, percent destroyed, and DRE for six compounds are given (refer to Section 5.1.1 for definition of terms). The results for the two highest boiling compounds are based on initial concentrations measured by GC/MS analysis.

The lowest boiling compounds (methyl naphthalenes) showed very little destruction although the ratio of 1-methyl naphthalene to 2-methyl naphthalene decreased by a factor of two to three. In addition, naphthalene, which was not found in the original soil, was produced in the process, presumably by partial reaction of higher homologs. Differences in reaction rates are also observed for the intermediate boiling aromatics (dimethyl naphthalenes, acenaphthene, fluorene, phenanthrene, in the boiling point range between 260 and 340°C.) These compounds show destructions ranging from about 50 to over 90% destroyed whereas some of the saturated hydrocarbons in the same boiling range (pristane and phytane) are generally present in the products at about 50% of the feed content.

Higher boiling aromatic hydrocarbons (pyrene, chrysene, benzopyrene, etc. with BP >340°C) are nearly completely destroyed with only very low levels, or nondetect levels, observed in any of the product fractions. This indicates that the process works well for the high boiling point compounds, even at temperatures below their boiling points.

Thus in Table 16 the recoveries of the four compounds that were quantified by the analytical method are representative of the yields observed semi-quantitatively for the other hydrocarbons with similar boiling ranges in the test soil. The effect of boiling range on the fate of the hydrocarbon contaminant in the soil, whether desorbed into the overhead, chemically destroyed, or left as trace residuals on the treated soil are similar to the initial screening studies in Section 5 on the effect of boiling range on the fate of contaminants in the process.

#### TABLE 16. ROTARY REACTOR TESTS - RECOVERIES

|                               | Run 46-6: 350°C, 1 hr, 6.9% S |          |                         |        |        |          |       |       |  |
|-------------------------------|-------------------------------|----------|-------------------------|--------|--------|----------|-------|-------|--|
|                               |                               | mg/kg mf | mg recovered/kg mf feed |        |        | Overhead | DRE   |       |  |
|                               | BP °C                         | feed     | reactor                 | trap 1 | trap 2 | Recovery | %     | %     |  |
| 2-methyl naphthalene          | 241                           | 58.9     | 0.09                    | 49.03  | 6.84   | 94.8%    | 5.0%  | 99.8% |  |
| acenaphthalene                | 278                           | 257.9    | 0.00                    | 19.87  | 0.74   | 8.0%     | 92.0% | >99.9 |  |
| phenanthrene                  | 340                           | 380.0    | 0.09                    | 46.09  | 5.30   | 13.5%    | 86.5% | >99.9 |  |
| nyrene                        | 393                           | 633.6    | 0.08                    | 3.90   | 0.00   | 0.6%     | 99.4% | >99.9 |  |
| chrysene                      | 448                           | 323      | 0.00                    | 0.00   | 0.00   | 0.0%     | >99.9 | >99.9 |  |
| benzopyrene/benzofluoranthene | >450                          | 680      | 0.00                    | 0.00   | 0.00   | 0.0%     | >99.9 | >99.9 |  |

|                               |       | Run 46-10: 350°C, 1 hr, 20% S |          |               |        |            |            |       |  |  |  |
|-------------------------------|-------|-------------------------------|----------|---------------|--------|------------|------------|-------|--|--|--|
|                               |       | mg/kg mf                      | mg recov | ered/kg mf fe | ed     | Overhead E | estruction | DRE   |  |  |  |
|                               | BP °C | feed                          | reactor  | trap 1        | trap 2 | Recovery   | %          | %     |  |  |  |
| 2-methyl naphthalene          | 241   | 58.9                          | 0.00     | 24.96         | 0.30   | 42.9%      | 57.1%      | >99.9 |  |  |  |
| acenaphthalene                | 278   | 257.9                         | 0.00     | 9.79          | 0.05   | 3.8%       | 96.2%      | >99.9 |  |  |  |
| phenanthrene                  | 340   | 380.0                         | 0.00     | 13.54         | 0.34   | 3.7%       | 96.3%      | >99.9 |  |  |  |
| pyrene                        | 393   | 633.6                         | 0.08     | 0.00          | 0.00   | 0.0%       | >99,9      | >99.9 |  |  |  |
| chrysene                      | 448   | 323                           | 0.00     | 0.00          | 0.00   | 0.0%       | >99.9      | >99.9 |  |  |  |
| benzopyrene/benzofluoranthene | >450  | 680                           | 0.00     | 0.00          | 0,00   | 0.0%       | >99.9      | >99.9 |  |  |  |

|                               | Run 46-14: 300°C, 1 hr, 11% S |          |                         |        |        |                      |        |       |
|-------------------------------|-------------------------------|----------|-------------------------|--------|--------|----------------------|--------|-------|
|                               |                               | mg/kg mf | mg recovered/kg mf feed |        |        | Overhead Destruction |        | DRE   |
|                               | BP °C                         | feed     | reactor                 | trap 1 | trap 2 | Recovery             | %      | %     |
| 2-methyl naphthalene          | 241                           | 58.9     | 0.00                    | 71.08  | 1.04   | 122.4%               | -22.4% | >99.9 |
| acenaphthalene                | 278                           | 257.9    | 0.44                    | 21.91  | 0.15   | 8.6%                 | 91.3%  | 99.8% |
| phenanthrene                  | 340                           | 380.0    | 1.07                    | 60.50  | 2.37   | 16.5%                | 83.2%  | 99.7% |
| nyrene                        | 393                           | 633.6    | 0.58                    | 0.00   | 0.00   | 0.0%                 | >99.9  | >99.9 |
| chrysene                      | 448                           | 323      | 0.00                    | 0.00   | 0.00   | 0.0%                 | >99.9  | >99.9 |
| benzopyrene/benzofluoranthene | >450                          | 680      | 0.00                    | 0.00   | 0.00   | 0.0%                 | >99.9  | >99.9 |

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#### Run 46-18: 350°C, 1 hr, 9.1% S mg recovered/kg mf feed Overhead Destruction DRE mg/kg mf feed trap 1 BP °C reactor trap 2 Recovery % % 31.9% 64.9% 1.90 18.00 0.79 96.8% 241 58.9 2-methyl naphthalene 1.56 11.20 0.00 4.3% 95.1% 99.4% acenaphthalene 278 257.9 98.5% 5.74 50.22 13.8% 84.7% phenanthrene 340 380.0 2.12 99.7% 393 633.6 1.99 0.00 0.00 0.0% 99.7% pyrene 0.00 0.00 0.0% >99.9 >99.9 323 0.00 chrysene 448 0.0% >99.9 >99.9 0.00 0.00 benzopyrene/benzofluoranthene >450 680 0.00

|                               | Run 46-22: 300°C, 0.5 hr, 10.4% S<br>ma/kg mf mg recovered/kg mf feed Overhead Destruction [ |       |         |        |        |          |         |       |
|-------------------------------|--|-------|---------|--------|--------|----------|---------|-------|
|                               | BP °C  | feed  | reactor | trap 1 | trap 2 | Recovery | %       | %     |
| 2-methvi naphthalene          | 241  | 58.9  | 0.88    | 115.57 | 1.93   | 199.4%   | -100.9% | 98.5% |
| acenaphthalene                | 278  | 257.9 | 0.00    | 0.00   | 0.00   | 0.0%     | >99.9   | >99.9 |
| phenanthrene                  | 340  | 380.0 | 0.89    | 59.09  | 2.99   | 16.3%    | 83.4%   | 99.8% |
| pyrene                        | 393  | 633.6 | 0.00    | 0.00   | 0.00   | 0.0%     | >99.9   | >99.9 |
| chrysene                      | 448  | 323   | 0.00    | 0.00   | 0.00   | 0.0%     | >99.9   | >99.9 |
| benzopyrene/benzofluoranthene | >450   | 680   | 0.00    | 0.00   | 0.00   | 0.0%     | >99.9   | >99.9 |

|                               | Run 46-26: 350°C, 0.5 hr, 11.1% S |          |                         |        |        |                      |        |       |
|-------------------------------|-----------------------------------|----------|-------------------------|--------|--------|----------------------|--------|-------|
|                               |                                   | mg/kg mf | mg recovered/kg mf feed |        |        | Overhead Destruction |        | DRE   |
|                               | BP °C                             | feed     | reactor                 | trap 1 | trap 2 | Recovery             | %      | %     |
| 2-methyl naphthalene          | 241                               | 58.9     | 0.69                    | 106.71 | 2.47   | 185.3%               | -86.4% | 98.8% |
| acenaphthalene                | 278                               | 257.9    | 0.38                    | 16.69  | 0.00   | 6.5%                 | 93.4%  | 99.9% |
| phenanthrene                  | 340                               | 380.0    | 0.96                    | 165.34 | 7.64   | 45.5%                | 54.2%  | 99.7% |
| pyrene                        | 393                               | 633.6    | 0.55                    | 6,53   | 0.00   | 1.0%                 | 98.9%  | >99.9 |
| chrysene                      | 448                               | 323      | 0.00                    | 0.00   | 0.00   | 0.0%                 | >99.9  | >99.9 |
| benzopyrene/benzofluoranthene | >450                              | 680      | 0.00                    | 0.00   | 0.00   | 0.0%                 | >99.9  | >99.9 |

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The weight gain in the caustic trap is presumed to be mainly hydrogen sulfide. Sulfur analyses of the caustic trap permit an independent calculation of the weight of hydrogen sulfide and higher quantities are inferred from the sulfur analyses. These differences may be due to other sources of sulfur products in the caustic trap such as polysulfides and carbon disulfide.

#### 7.3 DISCUSSION OF SOIL REACTOR RESULTS

The soil reactor showed nearly complete conversion for chrysene and benzopyrene, two compounds with boiling points above 400°C, and 99% conversion for pyrene. For lower boiling compounds, as anticipated, the soil reactor showed the effects of competition between reactions with sulfur, and desorption for the organic compounds. This section discusses the effects of varying the sulfur/soil ratio, the temperature and the residence time in the reactor.

#### 7.2.1 Sulfur/Soil Ratio

The initial experiment was conducted using only 6% sulfur, which was below the estimated stoichiometric requirement of sulfur of 10%. During this experiment, virtually all of the methyl naphthalene was recovered in the overhead products. When 20% sulfur as added, the percentage of methyl naphthalene recovered in the overhead product decreased to 35%, indicating significant reaction with the excess sulfur. When 10% sulfur was added, with the temperature maintained at 350°C, the results were mixed: one run showed 65% methyl naphthalene conversion, while a second showed negative conversions.

#### 7.3.2 Residence Time

Four of the six runs were conducted at one hour soil residence time. Two runs were conducted at 300°C, both using 10% sulfur in soil, with one hour and one-half hour residence times. Both runs showed overall DRE's above 99.5%

The half-hour run showed a greater amount of material in the traps, particularly acenaphthene and phenanthrene. This result appeared to be anomalous, except that it was duplicated when dual one hour and half hour runs were conducted at 350°C. One explanation was that most of the reaction occurred for the two compounds in the vapor phase, and the two compounds desorbed relatively slowly. It is possible that a significant amount of acenaphthene and phenanthrene desorbed after the reactor started to cool down, and therefore passed through the sulfur without reacting.

#### 7.3.3 Temperature

Runs were conducted at 300 and 350°C. The plans initially included runs at lower temperatures, to try to determine the lower limit of effectiveness for the process, because the evidence from gas flow and scrubber water discoloration indicated significant production of  $H_2S$  (and therefore, the initiation of the Sulchem reaction) beginning about 190°C. However, analysis of the results at 300°C indicated that little could be gained from decreasing the temperature below that point. Elevating the reaction temperature above 350°C was not considered practical, since it would likely require reactor skin temperatures well in excess of sulfur's boiling point of 440°C.

#### 7.4 VAPOR REACTOR PERFORMANCE

Most of the results obtained related to the performance of the overall reactor with respect to the original starting soil, which is appropriate since that is the purpose of the reactor system. However, the reactor system was essentially two joined reactors: a soil reactor and a vapor reactor. The soil reactor was intended to react contaminants in the soil with sulfur, and desorb the remaining organic contaminants. The vapor reactor was intended to destroy the desorbed organics by forcing them through a heated, baffled cylinder containing molten sulfur.

The vapor reactor was sized to provide a nominal residence time of between three and five minutes for the vapors emanating from the soil reactor. This nominal residence time was calculated based on estimated nitrogen purge flow rates and hydrogen sulfide production. Vapor flow through the vapor reactor consisted almost entirely of nitrogen while the reactor was cool. Then water vapor would flow through the reactor as the temperature of the soil rose to 100°C. The water vapor flow rate was anticipated to be relatively high, as the soil contained up to 20% moisture. The water was not anticipated to carry over many organics with it, since the organics volatilized at much higher temperatures. After the water vapor was forced off the soil, the flow rate would tend to decrease again. It would increase once more at or near the reactor temperatures, as some organics volatilized and others began to react to form hydrogen sulfide. Nominally, this would have produced conversions in the vapor reactor in the range of 40 to 75% (based on toluene vapor rate data in Section 5), at temperatures ranging between 300 and 350°C.

Unfortunately, in order to maintain sufficient pressure throughout the system and in the scrubber, the nitrogen purge gas flow rate had to be maintained at nearly 2 L/min (based on ambient temperatures). This reduced the residence time in the vapor reactor to approximately 2.5 minutes. Further reductions in residence time occurred because the MGP soil used in the experiment had a relatively high level of organics present, and therefore produced more hydrogen sulfide than originally anticipated, and because most of the hydrogen sulfide tended to be produced over an approximately 15 minute time span, rather than the half hour or hour residence time. Estimated residence times for the organic vapors in the vapor reactor tended to range between 40 and 100 seconds, therefore, with theoretical conversions of between only 11 and 35%.

Based on the results for acenaphthene and 2-methyl-naphthalene, both of which volatilize below 300°C and therefore would not be expected to show much conversion while within the soil, it appears that a significant fraction of the organic compounds were destroyed in the vapor reactor. The destruction rates were higher for reactions run at higher temperatures. This may be due to the rate of heating allowed by the reactor temperature control system, which tended to ramp up more quickly when the temperature of the reactor and therefore would be anticipated to raise the temperature of the reactor and the sulfur more while the compound were volatilizing.

A limitation on the vapor reactor was that it was heated at the same rate as the soil reactor. Therefore, if compounds volatilized without reacting significantly in the soil reactor because it was not sufficiently hot, then the compounds would be anticipated to flow through the vapor reactor without reacting as well. Thus, for example, any compounds which were steam stripped from the soil while the water was boiling off could conceivable pass through the vapor reactor while the sulfur,

which melts at 120°C, was still solid and unreactive. During the final run (Run No. 46-26), CHMR attempted to compensate for this by heating the vapor reactor side of the rotary reactor more quickly than the soil side. The results from the run were disappointing, however, and showed no affect of this operational change.

In order to compensate for the deficiencies in the design and increase the conversion in the vapor reactor, CHMR recommends two changes: a larger reactor volume to increase the vapor residence time; and a decoupled soil/vapor reactor system which will enable the vapor reactor to be maintained at reaction temperatures even as the soil is being heated, so that desorbed organics can react. However, based on the rotary reactor results and the previous vapor reactor study described in Section 5, CHMR believes that the vapor reactor should not be envisioned as the sole means of treating or destroying organics with boiling points below about 200°C. A secondary activated carbon or condensation system is likely to be necessary to destroy or remove the organic compounds from the vapor stream.

#### 7.5 CONCLUSIONS FROM ROTARY REACTOR RUNS

Based on the results of the rotary reactor runs, CHMR concluded the following regarding the feasibility of the Sulchem Process for the destruction of organic compounds.

- The rotary reactor completely or nearly completely destroyed compounds with boiling points above 350°C when operated at 300 or 350°C.
- The rotary reactor produced efficient destruction when operated with roughly the stoichiometric quantity of sulfur.
- The rotary reactor showed efficient desorption of compounds with boiling points below 300°C. A portion of these compounds were destroyed in the attached vapor reactor.
- The vapor reactor as configured could destroy a significant percentage of the desorbed organics. To increase destruction efficiency, CHMR recommends a larger vapor reactor (higher residence time) which is coupled with the soil reactor to better maintain it at reaction temperature.
- The soil reactor, coupled with the vapor reactor and a trap to condense water vapor and semi-volatile organics (boiling point range 100-200°C), is a technically effective means of treating soils contaminated with organic compounds. A more sophisticated trap/condensation system, coupled perhaps with activated carbon adsorption may be necessary to treat soils contaminated with volatile compounds.

#### 8.0 DETAILED PROCESS DESCRIPTION

The Sulchem Process is designed to provide destruction of hazardous organics while simultaneously stabilizing metals in contaminated soils. The Sulchem Process uses elemental sulfur, which reacts with the carbon in organic materials at moderately elevated temperatures to form an insoluble, inert carbon-sulfur amorphous solid. The contained heavy metals are immobilized through formation of insoluble metal sulfides.

The Sulchem Process's main process components include:

- A pre-reaction mixer where the soil and sulfur are mixed;
- A reactor in which the soil/sulfur mixture is heated sufficiently to react the organics with sulfur;
- A vapor phase reactor or reactor zone in which desorbed organics from the first reactor are further reacted with elemental sulfur;
- The off-gas handling system, which collects and treats condensable by-products and scrubs acid gases from the effluent vapors;
- A water treatment system which removes accumulated organic chemicals from the wastewater; and,
- A post-reaction treatment unit that recovers excess reagent and prepares the treated product to comply with on-site disposal requirements.

The system in its most basic form is shown schematically in Figure 1. The focus of the research was on the development of the system in order to better detail the process components and configurations.

This section provides a discussion of two key process subsystems which were the focus of the research: the soils reactor and the vapor reactor systems. Then the overall process configuration is discussed.

#### 8.1 SOIL PROCESSING

Soil pre-processing will include screening to remove oversized particles (probably those greater than 1-inch diameter), dewatering in applications in which it is necessary, and mixing of the soil with sulfur. Screening is anticipated to occur in a trommel screen, or other standard soil screening system. Dewatering may occur in a filter press, if required. The soil is anticipated to be mixed with sulfur in a soil scrubber, or other grinding type mixer. The soil will pass through the scrubber (which will also break up clumps) and into the reactor. For some applications, the soil may be scrubbed and mixed with sulfur before it is sieved. This will help break up clods, if it is required.

#### 8.2 SOIL REACTOR

CHMR considered three alternative soil reactor designs:

• Multiple screw conveyor system;

- Rotary soil reactor; and,
- Stationary furnace type reactor.

Each of these systems would be assumed to operate at approximately the same temperature, atmospheric pressure, and with downstream vapor processing of off-gases and desorbed organics. The advantages and disadvantages of each are discussed below.

#### 8.2.1 Multiple Screw Conveyor System

Under this system, a multiple Holoflite screw system or porcupine processor would be used to mix and agitate the soil in a chamber, while being heated internally with hot oil and/or molten salts. A vapor space would be provided above the reactor, and off-gases would leave the reactor through ports located above the soil.

The advantages to this system are that it provides good mixing of the soil and sulfur, and potentially good heat transfer through the Holoflite screws. The disadvantages include difficulties sealing the system, the potential for mechanical problems with the inter-meshing screw systems, difficulties heating a system using molten salts (both in terms of seal problems into the Holoflite system as well as in heating and maintaining the salts in the first place), and difficulties in maintaining seals at the soil inlet and outlet.

#### 8.2.2 Rotary Reactor

Under this system, an externally fired rotary reactor would be used as a soil reactor. The reactor would essentially be a long cylinder on a slight angle, which rotates at 1 to 5 rpm, which is heated either by natural gas, or by electric inductive coils to the appropriate reaction temperature. Soils would enter through one end of the reactor, and slowly pass down through the reactor and out the far end. The reactor would be sized to provide residence times on the order of 1 hour. The soil would enter the system through an interlocking dual door mechanism, in which a holding chamber is filled with soil, then sealed, and then a door opens to allow that soil to pass into the rotary reactor. (Such systems are used in rotary kiln incinerators to maintain a sealed system as solids are entered or removed.) Likewise, a similar interlocking system would be employed to remove the solids from the lower end of the rotary reactor. Vapors would leave the system through a rotating joint at the lower end of the reactor.

#### 8.2.3 Stationary Furnace Reactor

This reactor would be similar in design to the furnace type reactors used in coal coking operations. A soil/sulfur charge would be added to one of a series of stationary furnaces, the off-gases collected and treated, and the furnaces would be heated by indirect gas firing between each furnace. Soil would then be pushed out of the furnace and quenched, as it is in coking operations. This design presented several challenges, including collection of gases when the soil leaves the furnace and lack of mixing in the furnace. It may be appropriate for high residence time operations (i.e., eight or more hours), but was not deemed appropriate for the Sulchem process.

#### 8.2.4 Selected Reactor and Considerations

After evaluating the advantages and disadvantages of the three alternative basic reactor designs, CHMR selected the rotary reactor as the most promising, because it appeared to be among the simpler mechanically, while offering great flexibility during actual operations.

The major parameters which needed to be considered for the reactor were then:

- **Reactor size**, determined primarily by: individual reactor feed capacity, residence time, transportability requirements, and reactor freeboard (vapor space above soil);
- Method of heating, which was determined by: required reaction temperature, soil capacity and moisture level, and individual charge feed rates (if feed was semi-continuous);
- Equipment used for conveying soil into and out of reactor. Two basic alternatives existed: a screw type conveyance system and a door mechanism. Considerations included: seal requirements, nitrogen blanketing, soil type, and whether the feed could be semi-continuous.

CHMR based the overall system economics on two base cases: a 10-ton per hour unit and a 20-ton per hour unit. The other design parameters and assumptions made regarding the reactor are summarized in Table 17. The overall reactor size requirement was determined assuming a maximum one-hour residence time *after* the soil was heated to reaction temperature, with a nominal 150 second gas stream residence time.

| Table 17. Rotary Reactor Assumptions and Parameters |   |   |  |  |  |  |
|---|---|---|--|--|--|--|
| Parameter   | 10-ton/hour Reactor   | 20-ton/hour Reactor   |  |  |  |  |
| Residence Time                                      | 1 hour after soil heat up                                       | 1 hour <i>after</i> soil heat up                                |  |  |  |  |
| Vapor Residence Time                                | 150 seconds   | 150 seconds   |  |  |  |  |
| Transportability                                    | Truck mounted system  | Truck mounted system  |  |  |  |  |
| Diameter Limitation:                                | 7 feet  | 7 feet  |  |  |  |  |
| Number of modular<br>units:                         | 3   | 5   |  |  |  |  |
| Inlet Soil Conveyance                               | Continuous; screw type<br>from hopper to reactor<br>center-line | Continuous; screw type<br>from hopper to reactor<br>center-line |  |  |  |  |
| Outlet Soil Conveyance                              | Semi-continuous; sealed door mechanism                          | Semi-continuous; sealed door mechanism                          |  |  |  |  |
| Maximum Reaction<br>Temperature                     | 400°C   | 400°C   |  |  |  |  |
| Method of Heating                                   | Propane/natural gas   | Propane/natural gas   |  |  |  |  |

#### 8.3 SULFUR/VAPOR REACTOR SYSTEM

An originally envisioned, the Sulchem system would include first a soil reactor to destroy the organics and stabilize the metals in soil, then a sulfur/vapor reactor to destroy desorbed organics in the off-gas stream. However, four basic options exist for the vapor reactor:

- No vapor reactor at all -- condense the desorbed organic chemicals and treat them with the wastewater stream.
- Sulfur/vapor reactor incorporated into soil reactor -- allow excess freeboard space in soil reactor to try to react some of the desorbed organics with sulfur, then condense/treat the remainder. The desorbed organics would be assumed to react with the elemental sulfur present in the vapor space from volatilization from the soil.
- Separate liquid sulfur/vapor reactor -- Use a sulfur/vapor reactor system similar to that described and tested in Section 7, which reacts the desorbed organics with liquid sulfur in a slowly rotating, approximately plug-flow reactor. Then condense any unreacted organics with the water stream and treat.
- Separate sulfur vapor/organic vapor reactor -- Based on previous Sulchem testing, construct a system which reacts the desorbed organics with sulfur vapor. It is in theory possible to construct a system capable of reacting nearly 100% of the desorbed organics, thereby leaving only a trace of organics in the wastewater stream. However, high vapor residence times, high temperature and extensive sulfur vapor handling systems would be required.

Based on the results of the experimental work, in which the vapor reactor was shown to require relatively high residence times for very efficient destruction (on the order of 400 to 1,000 seconds residence time, depending on the temperature for 99% toluene destruction), it was decided that it would not be practical to use any of the first three options to target destruction of all of the desorbed organics. Therefore, it is assumed that condensation of the organics with the water or from the gas stream, followed by further treatment and/or disposal, will be required.

The first three options, may qualitatively be anticipated to yield different destruction efficiencies: the first will yield negligible destruction in the vapor phase; the second may be designed for 30 to 60% destruction of the desorbed organic vapors, and the third for 60 to 90% destruction. The actual efficiencies for the process depend on the vapor residence time, which is a function both of the size of the space available for contact between the volatilized organics and sulfur, and the overall flow rate of the vapor stream. This latter parameter, as was seen in Section 5.2.3 (c.f., Table 7), is mainly determined by the moisture content of the soil. Because all three of the liquid sulfur/vapor reaction options are anticipated to require *some* downstream removal and processing of organics, it was decided that the second option, which allowed for some reduction in organic flow without requiring an entire separate reactor system to accomplish it, would be the most reasonable alternative of the three.

The fourth alternative, a sulfur vapor/organic vapor reactor has the potential of destroying virtually all of the organic compounds, provided that sufficient

contacting time was maintained. CHMR does not have data concerning the reactor rates at temperatures above 500°C, but based on extrapolation of data from lower temperatures, residence times on the order of several hundred seconds would be required for complete reaction. If this is the case, then the complexity of a sulfur vapor reactor, and the required sulfur vapor handling system, could not be justified.

Therefore, CHMR based the overall system design on the use of a sulfur/organic vapor reactor incorporated into the design of the soil reactor. For this, CHMR assumed that it would ensure a minimum vapor residence time of 150 seconds, (which would yield a 50% conversion at 350°C, based on the toluene data), based on the maximum moisture content assumed for the soil.

#### 8.4 OFF-GAS HANDLING SYSTEM

The off-gas handling system is assumed to consist of two key units: a cooling/condenser system to cool the gas and condense the water vapor and desorbed organics; and a scrubbing system to remove the hydrogen sulfide. The hydrogen sulfide removed in the scrubber may be converted back to sulfur for reuse in the process using LO-CAT II<sup>™</sup> or other sulfur process. The off-gases may be filtered prior to the condenser using a cloth filter to remove large particles, if this is necessary based on the soil behavior in the reactor.

If cooling water is available on the site, CHMR anticipates using a water-cooled condenser system to cool the off-gases and condense the water vapor. If such water is unavailable on the site, CHMR may use an air-cooled system instead. Both systems will have to be designed to allow for the condensed liquids to be collected, and to minimize the possibility for sulfur vapors to condense and solidify on small heat exchanger tubes.

The off-gas would pass through the first condenser, in which its temperature would be reduced from 300° to approximately 80°C, to a second condenser, which will operate under refrigeration and will cool the off-gases to the range of 10°C, effectively condensing nearly all the water vapor and any desorbed organics.

The remaining gas, consisting primarily of nitrogen purge gas and hydrogen sulfide, but with low concentrations of water vapor and a trace concentration of carbon disulfide, will be fed through a scrubber associated with the patented LO-CAT II<sup>™</sup> process. This process can be licensed from ARI Technologies of Palatine, Illinois, LO-CAT II<sup>™</sup> removes hydrogen sulfide from gas streams using a chelated iron system, then oxides the sulfide to elemental sulfur, which is separated. The advantages to using a LO-CAT II<sup>™</sup> unit is that it will enable the sulfur in the hydrogen sulfide to be recycled and reused in the process, reducing sulfur costs and eliminating a stream requiring disposal.

#### 8.5 SOIL POST-PROCESSING

Based on the results from the current work, minimal post-treatment of the resulting soil will be necessary. Virtually all the organic compounds originally present in the soil are anticipated to be removed or destroyed by the process. The hot soil will be quenched using water condensed from the gas stream. The only additional components present in the soil are anticipated to be a small amount of an inert solid,  $CS_{0.56}$ , and unreacted elemental sulfur. Elemental sulfur is already a natural

component of soils, and therefore is not anticipated to present an environmental concern.

#### 8.6 WATER TREATMENT

As envisioned, the process will generate no wastewater streams; all the water originally driven off the soil will be used to cool and re-moisten the soil in the quench system. The condensed water from the primary reactor is anticipated to contain some residual organic compounds. These compounds will need to be removed and/or destroyed before the water is used in the quench system. Therefore, a water treatment system is required. There is a tradeoff between the requirements for the water treatment system and the sulfur/vapor reactor system: the more efficient the sulfur/vapor system, the fewer organic will be present in the wastewater for treatment, and *vice versa*. In order to evaluate this tradeoff for the purposes of process economic calculations, CHMR chose a relatively simple, straightforward water treatment system which relied on granular activated carbon (GAC) to remove most of the organic compounds. CHMR did not evaluate other potential alternatives, such as UV/oxidation technology or air flotation technologies, which may ultimately be less expensive than GAC.

The wastewater treatment system is envisioned to include two major process units: a filter to remove entrained particles from the water, and a GAC column to remove any remaining organics from the water stream. The filter solids are anticipated to include primarily unreacted sulfur,  $CS_{0.56}$ , some small soil particles and perhaps trace organics. Most likely, the solids could be re-mixed back into the soil and re-processed. The activated carbon will require periodic regeneration. The treated water will be used to quench the hot soil exiting the soil reactor. No wastewater disposal or discharge to a stream or POTW is anticipated from the process.

#### 9.0 PROCESS ECONOMICS

Process economics were estimated based on the system designed above using several alternative scenarios. Major site and process parameters which were varied include:

- Site size;
- Treatment system overall capacity;
- Individual reactor capacity (number of parallel reactors); and,
- Soil moisture content.

Table 18 summarizes the economic calculation as a function of these variables. In each case, the site was assumed to contain soil with 2.5% total organic content and heavy metals concentrations below 1000 mg/kg. The process was operated at 350°C. The distribution of organic compounds was assumed to allow for 90% destruction of the organic compounds while they were within the soil. The vapor space residence time was allowed to vary between 90 and 140 seconds to size the reactors so they would fit on a flatbed trailer. All components which came in direct contact with the process were assumed to be constructed of 316 stainless steel, at a total cost of \$10.00 per lb fabricated. Sulfur was assumed to cost \$0.05 per lb (\$0.11/kg). The LO-CAT II<sup>™</sup> System was assumed to be leased to the process, at a cost of \$350/ton (\$385/1000 kg) of sulfur recovered. The process was assumed to be operated 80 hours per week. Finally, the granular activated carbon (GAC) used in wastewater treatment was assumed to cost \$2.00 per lb (\$4.40/kg), including the cost of regeneration.

Capital costs were taken as the sum of the costs of the following major units:

- Site preparation;
- Soil pre-treatment;
- Reactor, including the reactor units, plus the associated heater, rotary mechanism, insulation, and inlet and outlet system;
- Heat exchangers/condensers;
- Soil post-processing;
- Water treatment (assumed to use activated carbon).

The capital costs associated with the LO-CAT<sup>™</sup> system were assumed to be included in the lease costs for the system, which were based on the amount of sulfur recovered.

Operating costs included the following major cost items:

- Personnel costs, including 3 personnel associated with excavation, 2 plant operators and 1 supervisor or safety officer at the plant during operating hours (80 hours per week), and 2 laboratory technicians each working 40 hours per week;
- Equipment leasing costs associated with the LO-CAT<sup>™</sup> system and excavation equipment;
- Consumables including sulfur (10% by weight in the soil, but 50% of which was assumed to be recovered by LO-CAT II<sup>™</sup>), activated carbon in the wastewater treatment plant, and analytical supplies;

| TABLE 18. Summary of Process Economics  |                  |                  |                  |                  |                  |                  |  |  |
|---|------------------|------------------|------------------|------------------|------------------|------------------|--|--|
| Parameter                               | Case 1           | Case 2           | Case 3           | Case 4           | Case 5           | Case 6           |  |  |
| Site Size<br>(tons)                     | 20,000           | 20,000           | 10,000           | 40,000           | 40,000           | 40,000           |  |  |
| System<br>Capacity<br>(tons/hr)         | 10               | 10               | 10               | 20               | 20               | 20               |  |  |
| Moisture<br>Content (%)                 | 14               | 7                | 14               | 14               | 14               | 7                |  |  |
| Number of<br>Reactors                   | 3                | 3.               | 3                | 6                | 4                | 3                |  |  |
| Amount of<br>GAC req'd<br>(lb/ton soil) | 13.4             | 12.8             | 14.6             | 14.0             | 14.7             | 14.0             |  |  |
| Total Capital<br>Cost                   | \$2.6<br>million | \$2.5<br>million | \$2.5<br>million | \$4.4<br>million | \$3.2<br>million | \$2.6<br>million |  |  |
| Operating<br>Cost/ton                   | \$104            | \$90             | \$113            | \$85             | \$85             | \$83             |  |  |
| Capital<br>Cost/ton                     | \$43             | \$43             | \$68             | \$37             | \$27             | \$22             |  |  |
| Total<br>Treatment<br>Cost/ton          | \$147            | \$133            | \$181            | \$122            | \$112            | \$105            |  |  |

- Utilities, including gas or propane to heat the system at \$6/million btu, water (for cooling), and electricity;
- Maintenance, at 5% of the capital cost per year; and,
- Start-up costs, at \$50,000 per site.

Other costs which were factored into capital costs included the cost of transportation and assembly of the equipment.

As can be seen in the table, total costs vary between \$105 and 181 per ton of soil (\$115 and \$199/1000 kg), depending on the site conditions and process parameters. A discussion of some of the key process cost factors is given below.

#### Site Size

As anticipated, there are returns to scale with the process, in both the operating and capital cost domains that yield a decrease in the cost per ton with increasing site size. In addition, the cost is strongly a function of contaminant concentration. Case 1 costs decrease to \$130/ton (\$143/1000 kg) when the contaminant concentration is reduced to 1% rather than 2.5%. Most of this cost is associated with a reduction of the amount of GAC needed from 13.4 lbs/ton (6.7 kg/1000 kg of soil) to approximately 5 lbs/ton (2.5 kg/1000 kg).

#### System Capacity

Increasing the system capacity (tons per hour) tends to increase the capital cost (since bigger equipment is needed) while lowering the operating costs (since the same number of operators can handle more material). For sites of 20,000 cubic yards or less, a plant capacity of 10 tons per hour seemed to be the most reasonable. For sites larger than 20,000 tons, a system capable of treating 20 tons per hour (18,000 kg/hr) yields a significantly lower cost.

#### Moisture Content

Moisture in the inlet soil is volatilized in the reactor, and must later be condensed out of the gas stream. Thus, moisture causes an increase in both the heating and cooling requirements for the reactor system. In addition, and perhaps more importantly, moisture increases the volume of gas which must be handled in the system, proportionally increasing the reactor size for the same vapor residence time. Because the reactor lengths were assumed to be constrained to 30 to 35 feet maximum (which could fit on a truck), the vapor residence times were adjusted downward for soils with high moisture levels. This decreased reactor capital costs, but increased operating costs since the organic vapor destruction efficiency in the reactor decreased, thereby requiring the water treatment system to remove more organics using expensive activated carbon. (Again, it should be noted that the use of GAC as the primary means of separating the organics from the condensed water was not necessarily the optimal choice. Rather it was done to show the expected tradeoffs between destroying the organic compounds in the sulfur vapor reactor before they condensed with the water vapor and destroying them after they condensed with the water vapor.)

System costs at two moisture levels were compared in the table; 7% and 14%. A decrease in moisture from 14 to 7% was shown to cause a decrease in overall costs of approximately 8%. Although this decrease in estimated costs was significant, it was not large enough to justify the addition of dewatering equipment to drive the moisture level of the inlet soil to the single digit ranger. The only case in which the use of such equipment may be justified is when the moisture level is above 20%.

#### Number of Reactors

This parameter was a function of both the unit reactor capacity and the specified vapor residence time. It was constrained by overall reactor size limitations, based on the requirement that the reactor fit onto a truck for transportability. In general, the analysis showed that costs were reduced by reducing the number of reactors. Cases 4 and 5 are identical except that six reactors were used under Case 4 and four were used under Case 5. Both sets of reactors were approximately 1,600 cubic feet (45 m<sup>3</sup>) in size. Case 5 was estimated to cost approximately 10% less than Case 4.

One major tradeoff which was seen repeatedly in the economic analysis was the tradeoff between reactor size, which affected overall destruction efficiency for the organic compounds, and the costs of downstream wastewater processing. The activated carbon costs under many of the cases represented 25 to 40% of the overall system operating costs. Thus, if there were a more economical means of removing the organic compounds from the wastewater stream, then the overall system cost could be decreased significantly.

One additional case was run, in which it was assumed that a large, fixed installation was built in which the entire reaction occurred in one soil reactor with a capacity of 10 tons/hr (9000 kg/hr). This scenario was otherwise identical to Case 1. Assuming a non-transportable plant with a scrap value of 40% of its original value after one year, the cost per ton of soil rose from \$147 to approximately \$160 per ton (\$176/1000 kg). Thus, no advantage was seen in dropping the constraints required by transportability and building a fixed installation.
## **10.0 CONCLUSIONS AND RECOMMENDATIONS**

The Sulchem process was shown to destroy certain polynuclear aromatic compounds in soil (particularly higher boiling compounds such as pyrene, chrysene and benzopyrene) in a reactor when operated at temperatures between 300° and 350°C. However, a reactor configuration capable of efficient destruction of a broader range of compounds was not obtained. This limitation may have been more due to limitations of the laboratory study, rather than inherent limitations of the technology. Specific conclusions from this laboratory study of the Sulchem Process are as follows:

- Destruction within the soil reactor was strongly correlated with compound boiling point:
  - organic compounds with boiling points above 350°C are essentially completely destroyed in the process (destruction > 99.5%);
  - organic compounds with boiling points in the range of 250 to 350° are partially destroyed. However, a significant quantity volatilize before destruction occurs;
  - organic compounds with boiling points below about 250° C primarily volatilize from the soil reactor before reaction can occur.
- A second stage sulfur/vapor reactor was shown to destroy a significant percentage of the organics desorbed from the soil reactor, thereby requiring subsequent treatment of the condensate produced;
- Metal stabilization in the treated soil (as measured by TCLP) is achievable for certain metals (particularly lead, cadmium, zinc, copper, and nickel) due to sulfide formation, with performance limits depending on the chemical form and concentration (e.g., typically lead below 10,000 mg/kg, cadmium below 1000 mg/kg);
- Remediation costs employing the Sulchem Process are estimated at \$105 to \$183/ton based on site size, reactor configuration, and processing rate.

Additional testing is recommended to demonstrate integration of the process components. Only very limited testing of reactor configurations or techniques to destroy volatilized organics were employed. CHMR recommends additional testing of vapor-phase organic reactors at higher temperatures (400°C or higher) and longer residence times. From this, the destruction efficiency (and its limits) need to be determined for an integrated soil/vapor reactor system.

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## APPENDIX A

# RESULTS FROM PARAMETRIC STUDIES CONDUCTED AT 250°C USING A VENTED STIRRED REACTOR

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#### TABLE A1 EFFECTS OF REACTOR PARAMETERS ON DESTRUCTION EFFICIENCY IN VENTED STIRRED REACTOR

#### Effect of Residence Time

|                   |           |           | Run #1 T  | emp C     | 250      |              |         | Run #2 T  | emp C     | 250      |            |          | Run #3    | Temp C    | 250      |            |          |
|-------------------|-----------|-----------|-----------|-----------|----------|--------------|---------|-----------|-----------|----------|------------|----------|-----------|-----------|----------|------------|----------|
|                   |           |           | s         | %         | 0.130435 |              |         | S         | %         | 0.130435 |            |          | 5         | 5%        | 0.130435 |            |          |
|                   |           |           | Т         | ime hrs   | 0.5      |              |         | <u>т</u>  | ime hrs   | 1        |            |          | 7         | lime hrs  | 2        |            |          |
|                   | Boiling   | Reactor   | RECOVERIE | S (in mg) |          | Per          | cent    | RECOVERIE | S (in mg) |          | P          | ercent   | RECOVERIE | S (in mg) |          | P          | ercent   |
| Compound          | Point (C) | Feed (mg) | Reactor   | Ice Trap  | Scrubber | Total ug Des | stroyed | Reactor   | Ice Trap  | Scrubber | Total ug D | estroyed | Rkr 30c   | 33-30-A1  | Scr 30b  | Total ug D | estroyed |
|                   |           |           |           |           |          |              |         |           |           |          |            |          |           |           |          |            | -        |
| bibenzyl          | 28        | 5 368.5   | 42.25     | 46.17     | 1.39     | 89.81        | 75.6%   | 59.13     | 73.06     | 0.98     | 133.17     | 63.9%    | 3.87      | 229.18    | 0.00     | 233.05     | 36.8%    |
| hexachlorobenzene | 322       | 2 327.5   | 6.24      | 11.31     | 0.54     | 18.09        | 95.1%   | 10.52     | 23.35     | 0.37     | 34.24      | 90.7%    | 8.60      | 204.42    | 0.36     | 213.37     | 42.1%    |
| anthracene        | 340       | 306.1     | 13.37     | 2.10      | 0.13     | 15.60        | 95.8%   | 13.91     | 5.14      | 0.08     | 19.13      | 94.8%    | 7.32      | 63.99     | 0.00     | 71.32      | 80.6%    |
| pyrene            | 393       | 3 175     | 17.76     | 19.16     | 0.00     | 36.93        | 90.0%   | 12.04     | 14.22     | 0.00     | 26.27      | 92.9%    | 2.56      | 6.88      | 0.00     | 9.44       | 97.4%    |
|                   |           |           |           | 3         |          |              |         |           |           |          |            |          |           |           |          |            |          |

#### Effect of Sulfur Loading

|     |                  |           |           | Run #1 T   | emp C     | 250      |            |          | Run #2 1  | femp C    | 250      |            |                 | Run #3    | Temp C     | 250            |            |          |
|-----|------------------|-----------|-----------|------------|-----------|----------|------------|----------|-----------|-----------|----------|------------|-----------------|-----------|------------|----------------|------------|----------|
|     |                  |           |           | s          | %         | 13.0%    |            |          | 5         | \$%       | 13.0%    |            |                 |           | S%         | 13.0%          |            |          |
|     |                  |           |           | Τ          | 'ime hrs  | 0.5      |            |          | 1 1       | Time hrs  | 1.0      |            |                 | . ·       | Time hrs   | 2.0            |            |          |
|     |                  | Boiling   | Reactor   | RECOVERIES | S (in mg) |          | P          | ercent   | RECOVERIE | S (in mg) |          | P          | ercent          | RECOVERIE | ES (in mg) |                | Р          | ercent   |
| l   | Compound         | Point (C) | Feed (mg) | Reactor    | Ice Trap  | Scrubber | Total ug D | estroyed | Reactor   | Ice Trap  | Scrubber | Total ug D | <u>estroyed</u> | Rkr_30c   | 33-30-A1   | <u>Scr 30b</u> | Total ug D | estroyed |
|     | ·                |           |           |            |           |          |            |          |           |           |          |            |                 |           |            |                |            |          |
|     |                  |           |           |            |           |          |            |          |           |           |          |            |                 |           |            |                |            |          |
| b   | ibenzyl          | 285       | 368.5     | 56.34      | 76.10     | 2.88     | 135.32     | 44.3%    | 23.26     | 63.22     | 0.68     | 87.16      | 28.5%           | 3.87      | 229.18     | 0.00           | 233.05     | 65.31%   |
| -{h | exachlorobenzene | 322       | 327.5     | 12.88      | 20.13     | 0.89     | 33.90      | 12.8%    | 8.19      | 22.69     | 0.16     | 31.04      | 11.8%           | 8.60      | 204.42     | 0.36           | 213.37     | 65.15%   |
| a   | nthracene        | 340       | 306.1     | 15.52      | 5.00      | 0.20     | 20.72      | 14.3%    | 7.88      | 5.69      | 0.05     | 13.62      | 9.4%            | 7.32      | 63.99      | 0.00           | 71.32      | 23.30%   |
| p   | yrene            | 393       | 175       | 7.17       | 6.61      | 0.10     | 13.87      | 12.5%    | 2.26      | 2.92      | 0.04     | 5.23       | 4.7%            | 2.56      | 6.88       | 0.00           | 9.44       | 5.39%    |

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# APPENDIX B

# QUALITY ASSURANCE/QUALITY CONTROL

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## APPENDIX B QUALITY ASSURANCE/QUALITY CONTROL

This appendix presents select quality assurance/quality control results from duplicate experimental runs and analyses. Table B-1 shows analytical results from duplicate analyses of samples from the heavy metals experiments in the vented stirred reactor for experiment 33-13. The results show relative percent differences below 15% for three of the four analytes.

| Metal Analyte | Method   | TCLP Result #1 | TCLP Result #2 | RPD |
|---------------|----------|----------------|----------------|-----|
| Cadmium       | EPA 6010 | 0.17           | 0.31           | 58% |
| Lead          | EPA 6010 | 0.41           | 0.46           | 11% |
| Nickel        | EPA 6010 | 0.35           | 0.31           | 12% |
| Zinc          | EPA 6010 | 4.60           | 4.85           | 5%  |

# TABLE B-1DUPLICATE HEAVY METALS RESULTS FOR 33-13

Results from TCLP analyses for lead conducted on split samples for which the TCLP extractions were performed at two separate laboratories (Microbac Laboratories and NETAC) are given in Table B-2. The results show good agreement for two of the three analyses.

| Experimental<br>Reference # | Microbac<br>Extraction<br>Result (mg/L) | NETAC<br>Extraction<br>Result (mg/L) | RPD | Action                      |
|-----------------------------|---|--------------------------------------|-----|-----------------------------|
| 56                          | 82.4                                    | 75.8                                 | 8%  |                             |
| 58                          | 77.1                                    | 57.9                                 | 28% | Reanalysis<br>(TCLP = 78.5) |
| 67 .                        | 30.3                                    | 32.0                                 | 5%  |                             |

 TABLE B-2

 DUPLICATE TCLP EXTRACTION RESULTS FOR LEAD ANALYSES

Table B-3 shows results from three sets of duplicate organics analysis. The table shows relatively good agreement (RPD's generally below 15%) for the duplicate analyses for experiments 30 and 31. The RPD's were all below the threshold limit of 15%, except for some of the higher boiling compounds, which were found in relatively low concentrations. The RPD's for Run #32 were relatively high. Subsequent review of the analyses for Run 32 indicated a possible error in the extraction for the second analysis, which may have biased the results. Therefore the first analysis was accepted. Corrective steps were taken to ensure that the error had not occurred previously and would not recur in subsequent analyses.

|                   | Run #30    |            |     | Run #31    |            |      | Run #32    |            |     |
|-------------------|------------|------------|-----|------------|------------|------|------------|------------|-----|
| 3                 | Analysis 1 | Analysis 2 |     | Analysis 1 | Analysis 2 |      | Analysis 1 | Analysis 2 |     |
| Analyte           | mg         | mg         | RPD | mg         | mg         | RPD  | mg         | mg         | RPD |
| mesitylene        | 225.5      | 224.0      | 1%  | 220.3      | 232.4      | 5%   | 199.6      | 243.8      | 20% |
| durene            | 249.3      | 254.6      | 2%  | 245.6      | 261.7      | 6%   | 184.8      | 245.8      | 28% |
| naphthalene       | 287.9      | 317.9      | 10% | 296.3      | 313.4      | 6%   | 212.9      | 280.2      | 27% |
| 2-Me naphthalene  | 276.9      | 302.7      | 9%  | 281.8      | 301.7      | 7%   | 190.6      | 269.2      | 34% |
| biphenyl          | 295.8      | 323.8      | 9%  | 298.4      | 323.5      | 8%   | 186.2      | 282.5      | 41% |
| bibenzyl          | 229.2      | 244.2      | .6% | 221.5      | 254.6      | 14%  | 128.3      | 228.8      | 56% |
| hexachlorobenzene | 204.4      | 99.3       | 69% | 96.5       | 136.2      | 34%  | 84.1       | 205.4      | 84% |
| anthracene        | 64.0       | 27.7       | 79% | 23.3       | 75.6       | 106% | 29.3       | 69.0       | 81% |
| pyrene            | 6.9        | 2.6        | 91% | 2.3        | 8.2        | 113% | 4.5        | 12.7       | 95% |

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### TABLE B-3 RESULTS OF DUPLICATE ANALYSES OF SCRUBBER WATER FROM VENTED STIRRED REACTOR RUNS