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Summary of Canister Overheating Incident at the Carbon Tetrachloride Expedited Response Action Site

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Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06 87RL10930

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MAR 10 1994 <i>Station #12</i>	11	ENGINEERING DATA TRANSMITTAL	Page 1 of <u>1</u> 1. EDT 600822
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2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) 200 West Area CC1₄ ERA	4. Related EDT No.: NA
5. Proj./Prog./Dept./Div.: 200 West Area CC1₄ ERA Project	6. Cog. Engr.: S. A. Driggers	7. Purchase Order No.: NA
8. Originator Remarks: Release and distribute document		9. Equip./Component No.: NA
11. Receiver Remarks:		10. System/Bldg./Facility: NA
		12. Major Assm. Dwg. No.: NA
		13. Permit/Permit Application No.: NA
		14. Required Response Date: 1/31/94

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
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1	WHC-SD-EN-TI-203		0	Summary of Canister Overheating Incident at the Carbon Tetrachloride Expedited Response Action Site	4	1,2	1,2	

16. KEY			
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Reason	Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN
1	1	Cog. Eng. S. A. Driggers	<i>[Signature]</i>	1-28-94	H6-04				
1	1	Cog. Mgr. G. C. Henckel III	<i>[Signature]</i>	1-28-94	H6-04				
		QA							
		Safety							
		Env.							

18. <i>[Signature]</i> 1-28-94 A. Driggers Signature of EDT Originator Date	19. _____ Authorized Representative Date for Receiving Organization	20. <i>[Signature]</i> 1-28-94 G. C. Henckel III Cognizant/Project Engineer's Manager Date	21. DOE APPROVAL (if required) Ltr. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments
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			ID Number (include revision, volume, etc.) WHC-SD-EN-TI-203, Rev. 0		
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5. Key Words vapor extraction, granular activated carbon, overheating APPROVED FOR PUBLIC RELEASE	6. Author Name: S. A. Driggers <i>S. A. Driggers</i> Signature Organization/Charge Code 81351/PU2BA	
7. Abstract This document summarized events relating to the granular activated carbon canister overheating event of June 3, 1993, at the 200 West Area Carbon Tetrachloride Expedited Response Action Project.		
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EXECUTIVE SUMMARY

On June 3, 1993, a canister containing granular activated carbon (GAC) overheated during vapor extraction activities at the Carbon Tetrachloride Expedited Response Action site near the 216-Z-9 Trench in the 200 West Area at the Hanford Site. The overheating incident resulted in a band of discolored paint on the exterior surface of the canister. Although there was no other known damage to equipment, no injuries to operating personnel, nor any releases of hazardous materials, the incident is of concern because it was not anticipated. The incident also poses the possibility of release of carbon tetrachloride and other hazardous vapors if it were to recur. All soil vapor extraction system operations were halted until a better understanding of the cause of the offnormal occurrence could be determined and controls implemented to reduce the potential for a recurrence.

A series of activities was initiated to determine the cause and potential effects of overheating, and to develop controls that would either prevent or mitigate the effects of a similar incident. Those activities included consultation with industry experts, laboratory testing and analysis, assessment of the potential for generation and release of toxic and hazardous gases, heat transfer modeling, bench-scale testing, and evaluation of methods to reduce carbon tetrachloride concentration in the gas stream prior to adsorption on GAC.

Discussions with industry experts were inconclusive. Several believe that the overheating was driven by the heat of adsorption during operations at 28,500 parts per million by volume (ppmv) carbon tetrachloride. Others believe that adsorption alone could not cause the overheating and that other exothermic reactions such as the hydrolysis of carbon tetrachloride or oxidation of other trace elements often present in the soil gas may have contributed to the event.

Laboratory analysis and bench-scale testing revealed that hydrolysis of adsorbed carbon tetrachloride can occur at 380 °F (and probably lower temperatures), that GAC begins to slowly oxidize at 480 °F, and that GAC fully loaded with carbon tetrachloride will begin to oxidize at 630 °F. Thermal testing of painted coupons demonstrated that temperatures ranging from 550 °F to 660 °F are required for the observed paint discoloring to occur. Analysis of the quench water removed from the canister revealed the presence of hydrochloric acid, which is indicative of carbon tetrachloride hydrolysis.

The hydrolysis of carbon tetrachloride can result in the formation of the toxic gas phosgene. An analysis was performed that concluded that phosgene was likely to have been generated, but probably was quickly converted to carbon dioxide and hydrochloric acid. Any phosgene not reacted would have been adsorbed onto the GAC and not released to the atmosphere.

Results of the laboratory and bench-scale testing show that the heat of adsorption alone is not sufficient to have caused discoloration of canister paint. It is, however, sufficient to have initiated an unspecified exothermic reaction in the canister. The temperature rise caused by adsorption is also sufficient to have initiated oxidation of methyl ethyl ketone, which is occasionally found in the soil gas in conjunction with carbon tetrachloride. The heats of these reactions, added to the heat of adsorption, may have

resulted in temperatures capable of initiating significant combustion of the GAC, which is clearly capable of discoloring the canister paint.

Results of bench-scale testing indicate that operating a vapor extraction system at a nominal carbon tetrachloride concentration of 1,000 ppm_v poses little if any risk and can proceed without the imposition of further controls. A temperature rise of only a few degrees Fahrenheit is expected, based on test measurements under these conditions.

Safe vapor extraction operations appear achievable at canister inlet carbon tetrachloride concentrations in the range of 10,000 ppm_v. The following actions and controls may be necessary to ensure stable operations at this concentration.

- Limit the ambient temperature of the GAC and the inlet gas stream temperature.
- Continuously or at least frequently monitor the inlet gas stream for concentrations of carbon tetrachloride and other organics that may be present in the soil gas.
- Establish concentration thresholds for these gases to prevent an unacceptable rise in temperature.
- Implement controls to maintain concentrations below the thresholds.
- Provide a means of monitoring to avoid exceeding safe design limits.
- Provide a means of cooling GAC after a period of loading.
- Provide a means of suppressing an overheated condition or conditions believed to be capable of causing overheating.

The bench-scale test results provide considerable assurance for operation at 10,000 ppm_v carbon tetrachloride with the controls noted above. However, conditions were never achieved during the testing that duplicated the incident in the field or allowed testing of overheating suppression methods. Consequently, it is prudent to recognize that an unidentified mechanism may have caused the initial event and could precipitate a similar one even at 10,000 ppm_v carbon tetrachloride. Although the potential for an incident is remote, the following additional precautions are recommended for consideration.

- Instrument the primary canister with an array of centerline thermocouples. These will provide an indication of operating performance under field conditions, confirm bench-scale predictions, and may provide some indication of offnormal conditions.
- Full-scale operation should include a gradual increase in carbon tetrachloride concentration to verify safe operation.

- Until an operational history is established that provides sufficient assurance that an overheating incident will not recur, an overheating suppression system should be provided. Without additional testing, the most conservative, and recommended, approach is water quenching.

If operation at elevated concentrations of carbon tetrachloride (greater than 10,000 ppm_v) is desired, additional bench-scale testing is recommended to establish safe operating thresholds for the various constituents and to test less conservative means of overheating suppression such as nitrogen flooding.

ACRONYMS

ARAR	applicable or relevant and appropriate requirements
ASTM	American Society for Testing and Materials
CCl ₄	carbon tetrachloride
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act</i>
DOE	U.S. Department of Energy
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ERA	Expedited Response Action
GAC	granular activated carbon
HEPA	high-efficiency particulate air
MEK	methyl ethyl ketone
ppm _v	parts per million by volume
RL	Richland Operations Office
VES	vapor extraction system
VOC	volatile organic compound

Metric Conversion Chart

The following conversion chart is provided to the reader as a tool to aid in conversion.

Into Metric Units			Out of Metric Units		
<i>If You Know</i>	<i>Multiply By</i>	<i>To Get</i>	<i>If You Know</i>	<i>Multiply By</i>	<i>To Get</i>
Length			Length		
inches	25.4	millimeters	millimeters	0.039	inches
inches	2.54	centimeters	centimeters	0.394	inches
feet	0.305	meters	meters	3.281	feet
yards	0.914	meters	meters	1.094	yards
miles	1.609	kilometers	kilometers	0.621	miles
Area			Area		
sq. inches	6.452	sq. centimeters	sq. centimeters	0.155	sq. inches
sq. feet	0.093	sq. meters	sq. meters	10.76	sq. feet
sq. yards	.0836	sq. meters	sq. meters	1.196	sq. yards
sq. miles	2.6	sq. kilometers	sq. kilometers	0.4	sq. miles
acres	0.405	hectares	hectares	2.47	acres
Mass (weight)			Mass (weight)		
ounces	28.35	grams	grams	0.035	ounces
pounds	0.454	kilograms	kilograms	2.205	pounds
short ton	0.907	metric ton	metric ton	1.102	short ton
Volume			Volume		
teaspoons	5	milliliters	milliliters	0.033	fluid ounces
tablespoons	15	milliliters	liters	2.1	pints
fluid ounces	30	milliliters	liters	1.057	quarts
cups	0.24	liters	liters	0.264	gallons
pints	0.47	liters	cubic meters	35.315	cubic feet
quarts	0.95	liters	cubic meters	1.308	cubic yards
gallons	3.8	liters			
cubic feet	0.028	cubic meters			
cubic yards	0.765	cubic meters			
Temperature			Temperature		
Fahrenheit	subtract 32, then multiply by 5/9	Celsius	Celsius	multiply by 9/5, then add 32	Fahrenheit

CONTENTS

1.0	INTRODUCTION	1-1
2.0	BACKGROUND HISTORY	2-1
2.1	BACKGROUND OF THE CARBON TETRACHLORIDE ERA	2-1
2.2	SUMMARY OF SOIL VAPOR EXTRACTION TECHNOLOGY AT THE HANFORD SITE	2-1
3.0	SUMMARIES OF TASK INVESTIGATION	3-1
3.1	BACKGROUND SUMMARY	3-1
3.1.1	Summary of Vapor Extraction Technology at the Hanford Site	3-1
3.1.2	Description of VES Conditions at the Time of the Incident	3-2
3.1.3	Disposition of the Overheated Canister	3-4
3.1.4	Discussions with GAC Experts, Manufacturers, Consultants, and Others	3-7
3.1.5	Discussion of a GAC Overheating Incident at the DOE Savannah River Site	3-10
3.1.6	Review of Prebid Discussions	3-12
3.1.7	Potential Applicable Engineering Controls	3-12
3.2	LITERATURE REVIEW	3-13
3.3	GAC EXPERT FINDINGS	3-13
3.4	LABORATORY ANALYSES AND BENCH-SCALE TESTING	3-14
3.4.1	Organic Analysis of Incident Well Headspace and GAC Sample	3-14
3.4.2	Thermogravimetric Analyses of GAC	3-15
3.4.3	Full-Scale Thermocouple Response Tests	3-15
3.4.4	Phase I Bench-Scale Adsorption Testing	3-17
3.4.5	Phase II Bench-Scale Adsorption Testing	3-20
3.4.6	Canister Paint Coupon Temperature Tests	3-22
3.5	CANISTER OVERHEATING INCIDENT HEAT TRANSFER ANALYSIS	3-23
3.5.1	Purpose of Heat Transfer Modeling	3-23
3.5.2	Heat Transfer Mechanisms and Unknowns	3-23
3.5.3	Bench-Scale Phase I Adsorption Test Results and Analyses	3-25
3.5.4	Bench-Scale Phase II Adsorption Test Results and Analyses	3-25
3.5.5	Possible Events Contributing to Overheating	3-26
3.6	POTENTIAL FOR PHOSGENE GENERATION	3-27
3.7	EVALUATION OF CARBON TETRACHLORIDE TREATMENT ALTERNATIVES	3-29
3.7.1	Existing GAC System	3-29
3.7.2	Thermal Oxidation	3-30
3.7.3	Condensation by Mechanical Refrigeration	3-30
3.7.4	Condensation by Liquid Nitrogen	3-30
3.7.5	Summary of Evaluated Alternatives	3-31
4.0	CORRELATIONS OF TASK INVESTIGATION CONCLUSIONS	4-1
4.1	CORRELATION OF PAINT DISCOLORATION WITH BENCH-SCALE TESTING	4-1
4.2	CORRELATION OF HEAT BALANCE WITH LABORATORY TESTING	4-2
4.3	ADDITIONAL HEAT FROM CHEMICAL REACTIONS	4-2
4.4	CHEMICAL ANALYSES OF SOIL GAS	4-3

CONTENTS (cont.)

4.5	CORRELATION OF BENCH-SCALE TESTING WITH THE OVERHEATING CANISTER INCIDENT	4-3
5.0	CONCLUSIONS AND RECOMMENDATIONS	5-1
5.1	CONCLUSIONS OF OVERHEATING INCIDENT STUDIES	5-1
5.2	RECOMMENDATIONS	5-3
6.0	REFERENCE	6-1

APPENDIXES:

A	DESCRIPTION AND BACKGROUND OF THE CANISTER OVERHEATING INCIDENT . .	A-1
B	REFERENCES PERTINENT TO THE CANISTER OVERHEATING INCIDENT	B-1
C	GAC EXPERT FINDINGS	C-1
D	RESULTS OF LABORATORY ANALYSIS AND BENCH-SCALE TESTING REGARDING THE CANISTER OVERHEATING INCIDENT	D-1
E	CANISTER OVERHEATING INCIDENT HEAT TRANSFER MODELING	E-1
F	POTENTIAL FOR PHOSGENE CREATION	F-1
G	EVALUATION OF CARBON TETRACHLORIDE TREATMENT ALTERNATIVES FOR THE CARBON TETRACHLORIDE ERA	G-1

FIGURES:

3-1	Construction Details of GAC-Filled Canister	3-5
3-2	Photographs of Overheated Canister	3-6
3-3	Full-Scale Thermocouple Response Test: GAC Temperature Versus Time	3-16
3-4	Bench-Scale Test Equipment Schematic	3-18
3-5	Peak Temperature Rise in Bench-Scale Tests Versus Inlet Carbon Tetrachloride Concentration	3-19
3-6	Temperature Profiles for GAC Column Bench-Scale Test at 10,000 ppm _v Inlet Carbon Tetrachloride Concentration	3-21
3-7	Summary of Temperatures Related to Overheating Incident	3-28

TABLES:

3-1	Rating of Heat Transfer Mechanisms	3-24
3-2	Adsorption Parameters as a Function of Inlet Carbon Tetrachloride Concentration	3-25
3-3	Reaction Heat Release and Relative Temperature Rise	3-27

1.0 INTRODUCTION

This report summarizes and discusses the findings regarding the overheating of a canister containing granular activated carbon (GAC) used for adsorbing carbon tetrachloride from soil gas at the Hanford Site carbon tetrachloride expedited response action (ERA) site. This report also draws conclusions and provides recommendations for operational limits for GAC-filled canisters and describes further work necessary to establish new operational limits that allow for optimal production under safe operating conditions.

The GAC-filled canister that overheated was being used to adsorb carbon tetrachloride vapors drawn from a well near the 216-Z-9 Trench, a subsurface disposal site in the 200 West Area of the Hanford Site. The overheating incident resulted in a band of discolored paint on the exterior surface of the canister. Although there was no other known damage to equipment, no injuries to operating personnel, and no releases of hazardous materials, the incident is of concern because it was not anticipated. It also poses the possibility of release of carbon tetrachloride and other hazardous vapors if the incident were to recur. All soil vapor extraction system (VES) operations were halted until a better understanding of the cause of the incident could be determined and controls implemented to reduce the possibility of a recurrence.

A series of activities was initiated to determine the cause and potential effects of overheating, and to develop controls that would either prevent or mitigate the effects of a similar incident. Those activities included consultation with industry experts, review of available literature, laboratory testing and analysis, assessment of the potential for generation and release of toxic or hazardous gases, thermal analysis of the incident, bench-scale testing, and evaluation of methods to reduce carbon tetrachloride concentration in the soil gas stream prior to adsorption on GAC. This report discusses these activities and findings, and correlates the conclusions. This report also offers specific recommendations for future activities that will enable restart of VES operations under safe conditions.

The focus of this report and the intent of all the activities associated with understanding the overheating incident has been to provide information that will allow safe restart of the VES operations, develop operational limits and controls to prevent recurrence of an overheating incident, and safely optimize recovery of carbon tetrachloride from the ground.

2.0 BACKGROUND HISTORY

This chapter contains a brief background of the Carbon Tetrachloride ERA and a concise discussion of the carbon tetrachloride soil vapor extraction technology.

2.1 BACKGROUND OF THE CARBON TETRACHLORIDE ERA

An ERA is a provision of the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) that allows accelerated cleanup activities to be undertaken at waste sites to abate imminent hazards or to prevent significantly increased degradation of the environment that might occur if action were delayed until completion of the remedial investigation/feasibility study and the record of decision.

In December 1990, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) requested the U.S. Department of Energy (DOE), Richland Operations Office to proceed with detailed planning, including nonintrusive field work required to implement the ERA for the carbon tetrachloride contamination in the 200 West Area. The request was based on concerns that the carbon tetrachloride residing in the soils was continuing to spread to the groundwater and if left unchecked, would significantly increase the area of groundwater contamination.

The carbon tetrachloride contamination is linked to past liquid waste disposal practices resulting from operation of Z Plant (now called Plutonium Finishing Plant) in the 200 West Area. Approximately 800 metric tons of carbon tetrachloride was discharged to three different sites from 1955 to 1973 (DOE-RL 1991). An initial site evaluation included a pilot test of a VES. Based on initial site evaluation and an engineering evaluation/cost assessment, soil vapor extraction with aboveground treatment was proposed as the preferred remedial alternative. In January 1992, EPA and Ecology authorized DOE to initiate soil vapor extraction technology for cleanup of the carbon tetrachloride in the unsaturated soils.

2.2 SUMMARY OF SOIL VAPOR EXTRACTION TECHNOLOGY AT THE HANFORD SITE

The carbon tetrachloride is recovered from the unsaturated soils by extracting contaminated soil gas through wells that are perforated at one or more intervals in the subsurface. Equipment at the surface is used to pull soil gas from the subsurface and treat it by adsorption to GAC to remove contaminants before it is released to the atmosphere.

A VES began operating at the 216-Z-1A Tile Field in February 1992. The tile field is one of three sites used for disposal of carbon tetrachloride between 1955 and 1973. Typical levels of carbon tetrachloride in the extracted soil gas from this area ranged from a few hundred to 1,000 parts per million by volume (ppm_v). More than 9 metric tons of carbon tetrachloride has been removed from this area by soil vapor extraction.

A second VES began operating at another disposal site, the 216-Z-9 Trench, in March 1993. The initial characterization tests conducted at this site in 1991 detected soil gas having carbon tetrachloride concentrations of several thousands parts per million. The soil gas concentrations were later found to increase to nearly 30,000 ppm, carbon tetrachloride based on the initial operational data from the VES. A third VES (a mobile unit) has also been operated at the 216-Z-9 Trench, beginning in May 1993. Characterization of one of the wells in the area of this disposal site was being performed when the overheating incident occurred on June 3, 1993. A more complete description of the incident is provided in the following chapter.

3.0 SUMMARIES OF TASK INVESTIGATION

Over the course of the investigation of the overheating incident, seven investigative tasks were performed. The key findings and conclusions of these tasks are summarized in this chapter. Additional detail on the task investigations is provided in Appendixes A through G.

3.1 BACKGROUND SUMMARY

This section describes the VES technology, the general background of the incident, and other relevant information collected during early phases of this investigation. This section provides specific information on the following topics:

- Description of vapor extraction technology at the Hanford ERA sites
- Description of VES conditions at the time of the incident
- Disposition of the overheated GAC canister
- Discussions with GAC experts, manufacturers, consultants, and others
- Discussion of a GAC overheating incident at the DOE Savannah River Site
- Review of prebid discussions with prospective bidders on GAC reactivation contract
- Summary of candidate engineering controls to preclude recurrence of overheating.

3.1.1 Summary of Vapor Extraction Technology at the Hanford Site

Vapor extraction technology has been deployed as part of an ERA to recover carbon tetrachloride from vadose zone sediments beneath the 200 West Area at the Hanford Site. Most of the carbon tetrachloride is believed to remain in the unsaturated soils beneath three disposal sites: the 216-Z-1A Tile Field, the 216-Z-18 Crib, and the 216-Z-9 Trench. The carbon tetrachloride is recovered from the soil by extracting soil gas containing carbon tetrachloride vapor. Access to the contaminated soil gas is typically provided through wells equipped with open intervals located 80 to 200 ft deep. A VES is used to apply a vacuum to the wells to draw the soil gas to the surface where it is treated. A typical VES at the Hanford Site consists of a cyclone to remove entrained water droplets that would otherwise damage downstream equipment, a high-efficiency particulate air (HEPA) filter to remove entrained particulate matter, a blower with a capacity of up to 500 ft³/min to extract the soil gas, a chiller to cool the gas, three GAC-filled canisters in series for adsorbing carbon tetrachloride and trace organics, and a stack for venting the treated gas to the atmosphere. Flow through the canisters is

downward, i.e., the soil gas enters the canister through an inlet at the top and exits at an outlet near the bottom.

The first GAC-filled canister encountered by the extracted soil gas is designated the "primary" canister. The primary canister provides the bulk of the carbon tetrachloride adsorption. This canister is followed in the series by a "secondary" canister and a "tertiary" canister. The secondary and tertiary canisters provide backup to give nearly complete removal of carbon tetrachloride from the soil gas and to ensure there are no releases to the environment above allowable limits.

Typically, a new canister is installed first in the tertiary position from which it moves stepwise to the primary position. After the primary canister is loaded with carbon tetrachloride it is removed from the treatment train for offsite reactivation. The former secondary canister is moved to the primary position, and the tertiary canister is moved to the secondary position.

The primary canister used during the overheating incident had served over a month earlier as the secondary canister during characterization of soil gas at several other wells at the 216-Z-9 Trench site. This canister contained about 40 lb of carbon tetrachloride and an unknown quantity of other trace organics when it was installed on June 3, 1993 as the primary canister in the treatment train. Earlier in the day a VES test was performed to characterize soil gas at another well location. Less than 1 lb of carbon tetrachloride was collected in the primary canister during that characterization test.

Each of the three GAC-filled canisters used in the overheating incident contained about 1,760 lb of Envirotrol (Sewickley, Pennsylvania) EI-410S 4 x 10 mesh virgin coconut shell-based GAC. The GAC bed within the canisters is approximately 4 ft in diameter and 5.4 ft tall. The canisters are constructed of carbon steel that is painted on the exterior surfaces and coated with epoxy on the internal surfaces. An uncoated 20-mesh stainless steel screen supports the GAC bed inside each canister. The vendor specifications for the exterior coating include a dry temperature resistance of 200 °F for both the primer (polyamide epoxy) and the paint (aliphatic polyurethane). The specifications for the interior coating (epoxy phenolic) include a dry temperature resistance of 225 °F.

3.1.2 Description of VES Conditions at the Time of the Incident

On the morning of June 3, 1993, one of the VES units used at the Hanford Site was put into service to extract and treat soil gas from well 299-W15-82. The purpose of this work was to accurately characterize the carbon tetrachloride concentration of the soil gas in the vicinity of the well. Previous characterization of vapor samples from the well had shown carbon tetrachloride concentrations ranging from 1,000 to 30,000 ppm_v. Soil vapor from well 299-W15-82 was being extracted and treated when the primary canister overheated. Overheating was discovered when an operator detected an abnormal odor and discovered a narrow band of discolored paint on the exterior of the canister.

At the time of the incident, the following conditions existed:

Time of extraction operations:	10:22 a.m. to 12:20 p.m., June 3, 1993
Vacuum level at blower:	100 inH ₂ O
Flow through canisters:	240 ft ³ /min
Soil gas temperature at GAC inlet:	About 69 °F
Pressure on outlet side of blower:	10 inH ₂ O
Ambient temperature:	85 °F
Relative humidity @ process temp:	30% (estimated)
Atmospheric pressure:	29.2 inHg
Weather conditions:	Sunny
Wind speed/direction:	5 mi/h, S 60° W (@12:35 p.m.)
Carbon tetrachloride concentration upstream of primary canister:	28,500 ppm _v (@10:45 a.m.)
Carbon tetrachloride concentration downstream of primary canister:	681 ppm _v (@10:45 a.m.)
Carbon tetrachloride concen- tration at the exhaust stack:	Less than 1 ppm _v

With the exception of the concentration measurements, the above information is recorded with an automatic data acquisition system.

On detection of the overheated canister, the system blower was immediately shut down manually by a technician. This was followed by closure of the valve between the well and the blower to shut off the flow of the soil gas. An air valve to the atmosphere was then opened upstream of the blower with the intent of allowing release of any pressurizing gas in the primary canister.

After shutdown of the VES was completed, emergency procedures were implemented. The Hanford Fire Department, among other organizations, was notified. After brief discussions about the nature of the overheated canister and its contents, the fire department began to spray the canister from two sides with a water mist to cool it down. Shortly after the spraying operation commenced, a noncontacting infrared thermometer was used to monitor the temperature of the canister in the vicinity of the paint discoloration. This measurement was 240 °F and was the highest temperature recorded at any time during the incident.

After several sprayings, the canister valves were closed and the process hoses were removed from the primary canister and placed in plastic bags. The canister was then moved by forklift to the center of the site yard. The upper canister valve was then opened slightly, with a noticeable release of pressure. After about 4 h of spraying the external surface of the canister

and taking temperature readings, the canister temperature appeared to stabilize at about 150 °F. The fire department personnel then departed.

Soon after the fire department personnel left the site, the VES technicians sensed that the external temperature of the canister may have been increasing. However, no measurements were made. Concurrently, discussions with a GAC manufacturer indicated that if the GAC inside the canister had reached ignition temperature, the only method for extinguishing oxidation of the GAC would be to fill the canister with water. Based on the best judgement of the project team, the decision was made to follow this advice. Thus, approximately an hour after the fire department personnel departed the site, they were requested to return to fill the canister with water. At that point, the noncontacting infrared thermometer indicated a temperature rise of about 10 °F since the previous measurement taken more than an hour before. This placed the surface temperature of the canister at about 160 °F.

The fire department personnel donned protective equipment and slowly fed water into the top inlet of the canister. The bottom outlet valve on the canister had earlier been closed and capped. After about 40 minutes, the water level reached the top inlet and the water flow was shut off. According to the fire department, approximately 600 to 700 gal of water was pumped into the canister. The amount of water required to fill an empty canister to the level of the upper outlet was calculated to be about 605 gal. During the filling period, minor amounts of condensed water vapor were noted escaping from the top outlet. The area around the canister was cordoned off and safety personnel monitored the breathing zone for chlorinated hydrocarbons. None were detected. The fire department personnel again departed from the site.

3.1.3 Disposition of the Overheated Canister

Construction details of the canisters used in the Hanford Site VES are shown in Figure 3-1. The canisters were manufactured by Aquatec Engineering and Supply, Inc. (Sulphur, Louisiana). Carbon-steel butterfly valves, with seals and stainless steel shafts, and aluminum quick-connect fittings were installed on both the inlet and the outlet ports of the canister.

The overheated canister showed a discolored streak at about 40% of the canister height. The roughly horizontal streak was about 8-in. wide and was about one-third the canister circumference in length. The darkest part of the streak was located approximately opposite the side of the canister with the inlet and outlet ports. The paint was discolored, but it did not blister or peel. Three photographs of the canister are provided as Figure 3-2, including a photograph of the canister taken immediately prior to water spraying of the exterior by the Hanford Fire Department.

As previously described, the overheated canister was filled with water following the overheating incident. On June 7, approximately 350 gal of water was drained from the canister and placed into polyethylene-lined 55-gal drums. The pH of the water was measured because it was theorized that if the heat within the canister had been high enough to decompose the carbon tetrachloride, then hydrochloric acid (HCl) could have been produced. The measured pH of this drained water was between 0 and 1. An additional 20 gal of water was later drained from the canister and placed in a polyethylene-lined 55-gal drum. The balance of the water that had been added to suppress the overheated

Figure 3-1. Construction Details of GAC-Filled Canister.

Figure 3-2. Photographs of Overheated Canister.

June 3, 1993 Chemical Reaction at 216-Z-98
(photograph property of Hanford Fire Dept.)

condition was absorbed by the GAC. There were no losses by leakage or evaporation.

The canister was refilled with water on June 8 to reduce the acidity and, thus, reduce the potential for corrosion of the canister itself. Approximately 350 gal of water was later removed and placed into polyethylene-lined 55-gal drums. This removed water exhibited a pH of 1.3 and will require further characterization to determine its appropriate disposal. No further flushing of the canister was done.

From June 25 through June 27, ambient air was passed through the canister, then through three other GAC-filled canisters in series to capture any VOCs that might be emitted from the canister. This operation was performed to dry out the GAC to allow sampling.

On June 27, the overheated GAC was sampled. Approximately 1 quart of GAC was removed for both analyses and for shipment to the GAC vendor, Envirotrol, Inc., for testing. There was no visual evidence of charring in the retrieved samples. The acidic rinsate was also sampled at this time.

On July 12, results of the testing of the GAC from the overheated area of the canister were received from Envirotrol, Inc. The GAC showed no evidence of either physical or chemical damage due to overheating. Additional detail on the examination and testing of the overheated GAC is provided in Appendix D.

The internal surfaces of the upper and lower quick connect hose fittings, constructed of aluminum, exhibited surface corrosion. It is assumed that the corrosion was a result of exposure to the acidic solution. The 20-mesh stainless steel screen (which supports the GAC bed) may also be corroded due to acid attack. It is not known if the canister, which is constructed of carbon steel with an interior epoxy coating, has been corroded.

Coupons of the canister steel, individually painted and epoxied to represent exterior and interior coatings, were tested for degradation when exposed to heat. A temperature range of 550 °F to 660 °F was required to discolor the exterior painted coupon, first to the cocoa-brown color and then to the dark-chocolate brown color observed during the overheating incident. The epoxy on the coupon coated to represent the canister interior peeled from the metal at 660 °F. More detailed information on the coupon testing procedure is provided in Appendix D.

3.1.4 Discussions with GAC Experts, Manufacturers, Consultants, and Others

Discussions were held via telephone with numerous GAC experts, manufacturers, consultants, and others who are familiar with GAC applications. The intent of these discussions was to gain insight and information into the cause of the canister overheating incident and suggestions for engineering controls regarding future operation of the VFS.

The following discussion presents the collected opinions of more than 12 GAC experts. As will be noted, there is a diversity of opinions on most matters relating to the cause of the incident and the proposed engineering

solutions to monitor, detect, and respond to possible overheating or ignition of the GAC or to prevent its recurrence.

Opinions regarding the cause of the overheating were divided into two basic beliefs

- The overheating was caused solely by heat of adsorption due to the high carbon tetrachloride concentrations.
- The evidence of overheated paint implies that oxidizable substances were present and that combustion occurred.

All of the experts consulted expressed the belief that an inlet soil gas carbon tetrachloride concentration limit of 1,000 ppm_v was safe. In addition, others offered safe limits of 3,000 ppm_v and 5,000 ppm_v.

Opinions regarding the need to monitor the soil gas for the presence of oxidizable substances were unanimous. The most frequently mentioned oxidizable compound of concern was methyl ethyl ketone (MEK). Levels of MEK suggested as potentially capable of contributing to unstable condition ranged from 100 to 500 ppm_v.

The ignition temperature of coconut-based carbon was discussed, with a consensus of about 570 °F.

Discussions regarding the average flow velocity through the canister is an important design parameter related to the cooling ability of the gas stream, indicating two diverse opinions:

- A flow velocity of 20 ft/min that existed at the time of the incident should be sufficient to provide adequate cooling.
- A design velocity of 50 to 100 ft/min is required to provide adequate cooling.

Discussions regarding the type and form of GAC indicated that some optimization of GAC performance might be achievable. Two types of GAC are commercially available: coconut-based GAC and coal-based GAC. Coconut-based GAC, the type used in the Hanford Site VES, has a lower ignition temperature than coal-based GAC (generally about 570 °F versus 840 °F). Coconut-based GAC has better retentivity for vapor-phase volatile organic compounds (VOCs) and, thus, is more effective as an adsorbent in this application. For application at the Hanford Site, the consensus was that coconut-based GAC was an acceptable selection. However, one expert suggested the use of coal-based GAC to raise the temperature at which GAC could ignite.

Some mention was made of the form of the GAC granules. As supplied, the granules are of random shapes. However, processes are available that produce pelletized carbon chips. According to two experts, pelletized GAC is more likely to produce uniform flow through GAC canisters than randomly shaped GAC. Opinions were divided on whether nonuniform flow could have occurred in the GAC canister. Thus, the value of pelletized GAC is debatable.

Opinions regarding the possibility of nonuniform flow are pertinent because they introduce the possibility of elevated localized temperatures.

There was an equal division of opinion about whether the design of the canister could promote the possibility of nonuniform flow. Those who suggested nonuniform flow as a possible cause indicated that the pattern of discolored paint, which was not uniformly horizontal and not a uniform color, could have been a manifestation of nonuniform flow.

The following paragraphs summarize the opinions of the same GAC experts regarding the application of various engineering controls.

The soil vapor carbon tetrachloride concentration must be diluted to reduce the inlet concentration to the canister, preferably with ambient air. Some suggestions also included automatic control of the dilution based on continuous measurement of the inlet concentration, as opposed to the current practice of manual control of the ambient air valve.

Opinions on the usefulness of thermocouples for monitoring internal GAC temperatures were divided. The efficacy of thermocouples relates to their ability to sense temperature excursions within the canister. Of those experts who recommended the use of thermocouples, two or three thermocouple units installed at different depths in the GAC bed were suggested. Objections to thermocouple use were based on the fact that GAC is an excellent insulator and for this reason a thermocouple may not detect a hot spot in GAC more than a few inches away.

The use of thermocouples requires a setpoint for interlocking and shutting down the process control system. Several suggestions were given for the setpoint. One expert suggested that a maximum temperature of 150 °F as the setpoint would limit desorption and protect the internal epoxy lining of the canister. Another expert suggested setting a limit based on a 25 to 30 °F temperature rise above the inlet flow stream temperature. It should be noted, however, that the outlet flow stream temperature may be significantly affected during startup by seasonal changes in ambient temperatures. A third expert suggested an internal maximum temperature limit of 240 °F. One expert who has conducted actual laboratory experiments on GAC columns has measured internal temperature rises of 77 to 85 °F at 10,000 ppm_v of VOC, and expected a rise of about 140 °F at 30,000 ppm_v of carbon tetrachloride.

Opinions on prewetting the GAC as a heat and temperature moderator were divided. There is some operating experience to draw upon. Prewetting provides water that both adsorbs to the GAC and occupies pore space capillaries. When heat is generated by adsorption of the carbon tetrachloride onto the GAC, the water serves as a heat sink due to its high specific heat and heat of vaporization. The capacity for adsorption of carbon tetrachloride is initially reduced by the adsorbed water; however, the carbon tetrachloride preferentially adsorbs and drives off the water to a great extent.

Most knowledgeable persons indicated that prewetting was useful and could be practically employed. This method was employed after an overheating incident at Savannah River, another DOE facility. At this site, the method has proved successful and predictable as to when the effect was depleted. To implement the prewetting option at the Hanford Site, a water supply system would have to be engineered, as no water supply system currently exists at the ERA site.

The introduction of additional humidity into the flow stream may also provide a heat sink within the GAC canister. Two experts expressed the opinion that decreased temperatures would be realized at the expense of some loss in carbon tetrachloride adsorption capacity, since water vapor is adsorbed by GAC.

Monitoring for the combustion products of GAC can be accomplished by measuring carbon monoxide (CO) changes in the outlet flow stream. Most experts recommended this option in combination with a water quenching system to flood the GAC bed in case of GAC combustion. Two levels of control were also suggested, one which attempts to reduce carbon monoxide generation by running strictly ambient air through the canister, and another level which floods the canister with water if carbon monoxide levels do not decrease after running ambient air through the canister.

Some suggestions were made by project personnel regarding splitting of the flow stream among three treatment trains in order to reduce the loading rate into each canister. However, it is apparent from heat transfer analysis that the heat of adsorption is directly related to concentration and would remain the same in the split streams. A possible solution is to use ambient air for dilution to reduce the concentration and increase flow. This safer level of reduced concentration and higher gas stream flow rates could be run through two or three GAC trains simultaneously.

Several suggestions regarding preadsorptive and postadsorptive cooling by blowing ambient air through the canister were made, with the intent of reducing residual heat in the canister. Preadsorptive cooling could be employed to remove heat due to solar heating during hot weather and excessive residual heat from previous operations. Postadsorptive cooling could be employed to remove heat in the GAC by the convective cooling capability of the ambient air passed through the canister. Relatively slow cooling by conduction through the canister walls would occur if no air flow was employed.

Most experts have indicated that the soil gas concentrations of carbon tetrachloride extracted from the 216-Z-9 Trench are excessive for direct adsorption onto GAC, both for economic reasons and because of the high heat of adsorption. Hence, pretreatment alternatives such as condensing and thermal oxidation were suggested. Section 3.7 of this report provides an evaluation of these technologies versus direct adsorption on GAC, the technology currently being used with the carbon tetrachloride ERA sites.

3.1.5 Discussion of a GAC Overheating Incident at the DOE Savannah River Site

A similar incident of GAC overheating occurred at the DOE Savannah River Site. The overheating occurred in the GAC polishing step of an offgas treatment system that was being demonstrated under a technology development program. This system was being used to extract soil gas containing about 5,000 ppm_v of perchloroethylene and about 800 ppm_v of trichloroethylene. The overheating was discovered an hour into the operation, after resuming operations following an overnight shutdown. The incident caused plastic fittings on the 55-gal canister to melt, which allowed a small discharge of GAC to the environment.

An analysis of the event and consultation with the GAC vendor resulted in the conclusion that the heat of adsorption generated during the previous day's run, coupled with the cessation of the gas flow and associated convective cooling caused a hot spot. The hot spot was believed to be due to the slow oxidation of perchloroethylene and trichloroethylene while the unit was shut down overnight. When the system was restarted, the flow of soil gas provided additional oxygen and fuel to exacerbate the exothermic reaction that was occurring. The large, sudden input of heat from the reaction melted the plastic fittings on the canister.

Operational changes instituted since the incident include adding 2 gal of water to the canister before beginning adsorption to act as a heat sink and running ambient air through the system overnight if the system ran the previous day. Solvent recovery operations were allowed to resume when the responsible Savannah River engineer was able to convince his management that he understood the nature of the problem and had implemented corrective actions to prevent a recurrence.

The incident was originally declared an offnormal occurrence, but was later downgraded to a nonroutine incident. This change in safety designation was made because of the research and development context in which the work was being performed. A committee established in accordance with a DOE-mandated procedure determined that the incident had occurred in a "research and development" environment. The Savannah River engineer stated that the incident would not have been downgraded if the extraction process at the Savannah River Site had been operating in an environmental remediation mode as was the VES at the Hanford Site.

The Savannah River engineer reported that discussions with the canister supplier and a private corporation that had experienced a similar overheating incident were the only external sources of information obtained for explaining the incident at the Savannah River Site. He also indicated that the GAC in the overheated canister was examined visually with no evidence of charring. No samples were sent to the GAC vendor for analysis. A desorption analysis on the GAC showed only the same compounds as present in the soil gas stream. The pH of water mixed with a sample of the overheated GAC was about 7.

The responsible engineer expressed his belief that the GAC was initially ignited, but was not sure that the GAC was burning at the time of the release of GAC particles through the plastic fitting. He also suggested that the carbon-oxygen reaction could occur at temperatures below the ignition temperature of the GAC.

In reference to the Hanford Site overheating incident, the Savannah River engineer expressed his preference for prewetting the GAC as a safety control since the water can be applied with no liquid waste produced. He also supports using thermocouples as an experimental tool to measure the internal temperatures of the GAC. He suggested significant dilution of the incoming carbon tetrachloride concentrations. He added that plans have been prepared to install catalytic oxidation for removal of the bulk of the contaminants from the flow stream at the Savannah River Site prior to polishing with GAC.

3.1.6 Review of Prebid Discussions

Several technical discussions took place between Westinghouse Hanford Company and prospective bidders prior to awarding a service contract for GAC regeneration. An investigation was conducted of the records of these discussions to determine if operational limits or controls were suggested of which the VES project team was not aware.

These investigations revealed that all prospective bidders were under the impression that the 1,000 ppm_v limit, as specified in the GAC service contract statement of work, was typical of concentrations to be expected at all extraction sites. As a result, no bidder specified operational limits or controls.

Since the overheating incident, one technical representative made statements to the effect that the potential for a GAC bed fire was discussed during the procurement process for the GAC service contract. To date, no documentation that speaks directly to this discussion has been found.

3.1.7 Potential Applicable Engineering Controls

Based upon the accumulated information from the investigation of the GAC overheating incident, the following engineering controls were identified as features of the VES that can reduce the possibility of a recurrence of an overheating incident.

- Providing methods and controls to limit soil gas inlet carbon tetrachloride concentrations. This could include dilution using ambient air by manual or automatic methods.
- Providing internal GAC thermocouples to determine if temperatures generated by the heat of adsorption as the adsorption front passes each thermocouple are becoming excessive. The thermocouples may be ineffective for detecting hot spots.
- Providing a carbon monoxide/carbon dioxide monitor to detect the onset of significant GAC oxidation. A water dousing system or inert purge gas could be provided to extinguish a GAC combustion that could not be prevented by ambient air dilution.
- Providing prewetting to add a significant heat sink to the GAC bed. The prewetting may be effective for controlling the temperature rise within the GAC bed during adsorption of carbon tetrachloride. It is not known if prewetting will detrimentally affect the efficiency of carbon tetrachloride adsorption.
- Providing increased humidity in the flow stream before it enters the GAC, to serve as a heat sink during adsorption of carbon tetrachloride. This control may impact the loading capacity of the GAC.
- Providing preadsorptive and postadsorptive cooling by passing ambient air through the canisters. Preadsorptive cooling can remove residual heat that arises from solar heating or from

previous adsorption operations. Postadsorptive cooling can remove heat from the canister considerably faster than the current method, which relies on conductive heat transfer through the GAC to the canister walls.

- Providing pretreatment to reduce concentrations of carbon tetrachloride in the soil gas, leaving the canisters in the role of adsorbing relatively low concentrations. Certain options require handling and disposition of liquid carbon tetrachloride.

3.2 LITERATURE REVIEW

A literature search was conducted to locate published information on GAC adsorption. The results of this search are contained in Appendix B. This effort yielded journal articles, American Society for Testing and Materials (ASTM) standards, and technical literature from GAC vendors and manufacturers on the following topics:

- Theoretical modeling of the heat effects within canisters
- Experimental work identifying adsorbed organic compounds that readily oxidize to generate hot spots in GAC and quantifying the oxidation initiation temperatures
- Information on different types of GAC and adsorption isotherms for carbon tetrachloride on GAC
- Standard test methods for quantifying GAC parameters.

Several articles discussed GAC overheating incidents. Information on the causes and handling of these incidents, including postincident engineering and operational controls for overheating, was compiled. Very little quantitative information was found. Two articles citing experimental work on hot spot generation in GAC were also reviewed. Organic compounds that tend to cause hot spot problems and their reaction initiation temperatures were identified.

Several articles on mathematical modeling of GAC adsorption were found. The models were very complex, restricted to ideal situation, and required large amounts of computer time to solve. A review of GAC standard test methods provided an understanding of the interrelationships of important GAC parameters.

3.3 GAC EXPERT FINDINGS

A recognized expert in GAC adsorption was contracted to review the GAC overheating incident. The review consisted of a week-long discussion on the overheating incident, review of operating procedures and analytical data, and a site visit. Conclusions from this review are listed below.

There was no GAC "fire" based on the analytical data and historical statistics. Onsite personnel properly handled the incident. The overheating was not caused strictly by carbon tetrachloride adsorption; oxidizable

compounds in the soil vapor must be suspected. The soil gas was not sufficiently characterized prior to the incident.

It is the opinion of the expert that there is always some risk inherent in adsorbing soil gas onto GAC. Adsorption onto GAC is complex and at times may be unpredictable. The risks are acceptable if proper controls are in place.

The expert recommended that the following actions be taken:

- Performing bench-scale tests to quantify heat of adsorption and temperature profiles, to identify the heat effects of MEK and water vapor, and to determine what parameters should be measured to ensure system control
- Performing a thorough analysis of the compounds adsorbed on the GAC of the overheating incident
- Obtaining a representative sample of the soil gas from the incident well by operating the VES
- Identifying the conditions required for acid-generating reactions by laboratory testing.

Additional information on the expert review is provided in Appendix C.

3.4 LABORATORY ANALYSES AND BENCH-SCALE TESTING

This section summarizes the results of a number of laboratory analyses conducted during the investigation of the GAC overheating incident. Analyses were made of soil gas samples from the incident well headspace and a sample of the GAC from the overheated canister. Several laboratory thermogravimetric analyses were performed on the GAC as well.

Full-scale testing was performed to evaluate the effectiveness of thermocouple temperature measurement in a GAC bed as well as the heat sink effect of adsorbed water. In addition, bench-scale adsorption tests covering inlet carbon tetrachloride concentrations from nominal 1,000 to 30,000 ppm, measured peak temperatures and temperature profiles during adsorption in a GAC column. Exterior canister paint coupons were tested in an oven to determine the temperatures at which discoloration occurred during the overheating incident.

3.4.1 Organic Analysis of Incident Well Headspace and GAC Sample

An organic analysis for compounds other than carbon tetrachloride was conducted on the incident well headspace soil vapor and overheated GAC found only part per billion by volume levels of organic compounds including MEK (Appendix D). These concentrations were judged unlikely to be significant with respect to heat generation by either adsorption or oxidation reaction. Subsequent discussions with experts revealed that competitive adsorption can cause relative concentrations of 50% to 100% of inlet concentrations.

Specific methodology of the well head space analysis is provided in Appendix D. The analysis consisted of collecting a gas sample from the incident well using a sampling pump, at the desired elevation, passing the gas through an adsorption tube. The tube was then thermally desorbed into a gas chromatograph and analyzed for individual compounds by mass spectrometry.

The samples obtained from the incident well headspace may not have been representative of the soil vapor composition that existed at the time of the incident. The low-volume sampling method employed may not have obtained a sample representative of the high-volume VES operation. In the case of the GAC sample taken from the incident canister, the high temperature may have desorbed some compounds of concern, rendering it nonrepresentative as well.

Specific methodology of overheated GAC analysis is provided in Appendix D. A validated GAC desorption procedure was used to desorb organics and inorganics from GAC particles into a Tedlar (SKC West Corporation, Fullerton, California) bag. The samples are then collected by passing the gas through adsorption tubes. The tubes are thermally desorbed into a gas chromatograph and analyzed for individual compounds by mass spectrometry.

The physical characteristics are evaluated according to specific ASTM procedures. These procedures are ASTM D-2854 (apparent density), ASTM D-3467 (carbon tetrachloride activity), and ASTM D-3802 (hardness).

3.4.2 Thermogravimetric Analyses of GAC

Thermogravimetric analysis indicated that an exothermic reaction probably involving adsorbed carbon tetrachloride appears to begin at around 300 °F and that virgin GAC begins to slowly oxidize at around 480 °F. Carbon tetrachloride-loaded GAC begins to oxidize at about 630 °F. Both water and carbon tetrachloride desorbed at constant rates over the temperature range from 80 °F to 570 °F.

The heat of adsorption of carbon tetrachloride was not quantified, but was determined to decrease as GAC loading increased. Theoretically, more active adsorption sites with a corresponding higher heat of adsorption are loaded first, followed by less active sites with lower heat of adsorption.

3.4.3 Full-Scale Thermocouple Response Tests

An unused GAC-filled canister was instrumented with thermocouples embedded in the GAC and at the canister inlet and outlet. Heated air was blown into the canister. Air and GAC temperatures as well as inlet and outlet relative humidities were measured.

A thermal wave related to the heating of the GAC and to the desorption and subsequent re-adsorption of water was observed through thermocouple readings. Analysis of the data showed that large temperature gradients develop in the GAC and are measurable as shown in Figure 3-3. Gradients of 30 °F over a few inches of GAC were observed.

Figure 3-3. Full-Scale Thermocouple Response Test:
GAC Temperature Versus Time.

Adsorbed water was shown to provide a significant heat sink. About four times as much heat was required to desorb 5% adsorbed water as was required to heat the GAC from 80 °F to 130 °F.

Convective heat losses from the wall of the canister were estimated to be approximately 5% of the total heat input.

3.4.4 Phase I Bench-Scale Adsorption Testing

From August 4 to August 18, 1993, Phase I laboratory bench-scale tests were performed on the adsorption of carbon tetrachloride on GAC in the environmental engineering laboratory at Washington State University. The purpose of the testing was to investigate temperature rises associated with the adsorption of various concentrations of carbon tetrachloride and relate the results to the full-scale operation.

The testing apparatus used for the carbon adsorption consisted of a 3-in.-diameter by 6-ft-long carbon steel column (Schedule 40 pipe). The column was instrumented to measure temperatures at various column heights and to monitor the temperature, flow rate, carbon tetrachloride concentration, and relative humidity of the inflowing gas. A schematic of the bench-scale test apparatus is provided in Figure 3-4.

During the bench-scale testing, a number of runs were made varying the inlet concentration of the carbon tetrachloride from 1,000 to 30,000 ppm_v. The flow rate was maintained constant for all runs at a velocity equivalent to the velocity of the VLS canister operating at 500 ft³/min. The temperature rise experienced by the GAC column was automatically recorded on a minute by-minute basis. Results from this testing are discussed below.

- Over a range of carbon tetrachloride concentration of 1,000 ppm_v to 30,000 ppm_v, the maximum temperature rises in the column at simulated design flows was closely proportional to concentration, as shown in Figure 3-5.
- The maximum internal temperature reached was 270 °F. This was at design flow and a nominal carbon tetrachloride concentration of 30,000 ppm_v.
- The test at a nominal concentration of 30,000 ppm_v carbon tetrachloride did not produce an acidic GAC extract.
- Peak temperatures at each thermocouple location in the column were relatively constant as the thermal wave passed through the column.
- The width of the thermal wave increased as a function of depth in the column.
- The maximum temperature reached in the nominal 30,000 ppm_v carbon tetrachloride test was insufficient to discolor the paint to the extent experienced during the overheating incident.

Figure 3-4. Bench-Scale Test Equipment Schematic.

Figure 3-5. Peak Temperature Rise in Bench-Scale Tests Versus Inlet Carbon Tetrachloride Concentration.

- Significant temperature gradients can exist in the canister. During the nominal 30,000 ppm_v carbon tetrachloride test, a temperature gradient of over 108 °F existed over a depth of 31 in.
- The presence of 200 ppm_v MEK in the flow stream at 1,000 ppm_v carbon tetrachloride had no significant effect on the temperature rise in the column. The temperatures in the column were well below the 210 °F oxidation initiation temperature for MEK.
- The presence of 200 ppm_v MEK in the flow stream at 5,000 ppm_v carbon tetrachloride increased the internal temperature rise by approximately 5 °F. The temperatures in the column were well below the 210 °F oxidation initiation temperature for MEK.
- The outlet temperature did not reflect the temperature increases within the canister, e.g., when the peak temperature within the GAC-filled column is 50 °F over ambient, the outlet temperature only increases by 10 to 20 °F.

3.4.5 Phase II Bench-Scale Adsorption Testing

From November 8 to November 19, 1993, the Phase II bench-scale tests were performed at the Washington State University environmental engineering laboratory. These tests were performed as a followup to the Phase I tests discussed in the previous section. The purpose of these tests was three-fold: (1) to provide experimental data that directly relate to operation of the VFS at concentrations of 10,000 ppm_v of carbon tetrachloride with other solvents present, (2) to determine if a high concentration of carbon tetrachloride adsorbing onto GAC is sufficient to produce a temperature rise similar to that experienced during the overheating incident, and (3) to implement and test heat suppression methods that are suitable for field use.

The test setup and conditions were modified slightly from the Phase I testing as shown in Figure 3-6. Additional thermocouples were added to the test column at the 28-in. level to measure temperatures radially outward from the center of the column. Additional piping was added to allow the simultaneous injection of up to four gases (i.e., carbon tetrachloride, MEK, methylene chloride, and chloroform) into the column. Two heat suppression systems were added, the first being a nitrogen purge and the second being a water flush.

Significant results from the Phase II study are listed below:

- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 200 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 153.4 °F (an approximately 80 °F temperature rise above the inlet temperature).
- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 500 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 153.2 °F (an approximately 80 °F temperature rise above the inlet temperature).

Figure 3-6. Temperature Profiles for GAC Column Bench-Scale Test at 10,000 ppm_v Inlet Carbon Tetrachloride Concentration.

- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 1,000 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 164.7 °F (an approximately 95 °F temperature rise above the inlet temperature).
- Prewetting the GAC column lowered the maximum temperature from 153.4 °F to about 143 °F, a decrease of 10 °F. The effect of prewetting on other factors, such as adsorption efficiency, is unknown.
- The maximum temperature achieved with a carbon tetrachloride concentration of 40,000 ppm_v was 473.5 °F, a rise over the inlet temperature of approximately 405 °F. (The flow of carbon tetrachloride was interrupted for approximately 7 min, which may have impacted this test.)
- The maximum temperature achieved with a carbon tetrachloride concentration of 55,000 ppm_v was 445 °F, a rise above the inlet temperature of 375 °F. This is 30 °F lower than the peak temperature of the 40,000 ppm_v carbon tetrachloride test.
- An excessive temperature condition was never reached during these tests.
- The pH testing performed on the spent GAC from each of the tests resulted in pH values ranging from 9.18 to 10.13, indicating that little or no hydrolysis of carbon tetrachloride occurred.
- Heat suppression systems could not be tested because temperatures associated with oxidation could not be achieved in the test column.

3.4.6 Canister Paint Coupon Temperature Tests

The GAC canister paint coupon test indicated that a relatively high temperature of 550 °F is required to begin to darken the exterior canister paint and that approximately 660 °F is required to darken the paint to the darkest color observed in the overheating incident. The coupon results correlated well with results of a similar test on an actual exterior paint sample taken from a canister that had not overheated.

These temperatures were not achieved during bench-scale testing at even the highest carbon tetrachloride concentration. Hence, other phenomena such as chemical reactions, flow anomalies, or hot spots are likely responsible for producing the additional heat and higher temperatures needed to discolor the canister paint.

Interior epoxy coupons blistered and peeled at temperatures lower than 500 °F, the low end of the paint discoloration range. Hence, the interior epoxy coating of the incident canister probably disintegrated during the overheating. If so, the interior walls of the canister were subjected to acidic conditions and corrosion.

3.5 CANISTER OVERHEATING INCIDENT HEAT TRANSFER ANALYSIS

This section provides a discussion of the significant factors contributing to the temperature rise in the GAC canister during the overheating incident. Several methods were used to evaluate and quantify temperature rises associated with adsorption of carbon tetrachloride on GAC. Additional information on the GAC heat transfer analysis is provided in Appendix E.

3.5.1 Purpose of Heat Transfer Modeling

The mechanisms effecting heat transfer on GAC are complex, dynamic, highly interactive, and therefore difficult to model. Numerical three-dimensional models are available that can simulate the adsorption of carbon tetrachloride on to GAC (see Section 3.2). These models use a combination of mass transfer and heat balance equations to simulate this unsteady-state phenomenon. A review of these models has determined their application to the GAC overheating incident is not feasible based on the following:

- The assumptions necessary for modeling are numerous and cannot account for unanticipated behavior.
- Unanticipated behavior, particularly the possibility of chemical reactions, is considered to be a significant factor in the overheating incident.
- Extensive laboratory calibration testing would be required to validate the model.

As a result of this review, a less rigorous analysis method using an energy balance approach was selected to model the GAC overheating incident. An energy balance approach offers several advantages over the three-dimensional models: (1) it requires much less time to implement and the results can be quickly validated by a laboratory study and (2) the sensitivity of various parameters can easily be calculated. Disadvantages of this method are (1) the overheating incident cannot be modeled as a function of time, and (2) it assumes the heat of reaction equations are cumulative, which may not be accurate.

3.5.2 Heat Transfer Mechanisms and Unknowns

Interrelated mass and heat transfer mechanisms occur in the bed. These mechanisms occur simultaneously and can compete with each other during the adsorption process. Listed in Table 3-1 are the 15 known mass and heat transfer mechanisms that occur during GAC adsorption and their probable relative importance with respect to the overheating incident. A detailed discussion of these mechanisms is provided in Appendix E.

The mechanism that causes the initial temperature rise during adsorption is the heat of adsorption. Adsorption on GAC occurs in a mass transfer zone or front that slowly moves through the canister as demonstrated by the wave phenomenon discussed in the bench-scale tests (Section 3.4.4). This zone is considered to be a horizontal, cross sectional slice of the GAC bed normal to the direction of flow. Convective heating and cooling of the gas stream,

Table 3-1. Rating of Heat Transfer Mechanisms.

Mechanism	Relative importance
1. Heat of adsorption of carbon tetrachloride	High
2. Heat of adsorption/desorption of water vapor	High
3. Convective heating of gas stream	High
4. Convective cooling of gas stream	High
5. Conductive heat transfer between particles	Low
6. Conductive heat transfer within a particle	High
7. Convective mass transfer from gas to particle	High
8. Diffusive mass transfer into pores	Low
9. Rate of adsorption of carbon tetrachloride	Low
10. Conductive heat transfer to wall (pipe or canister)	Low
11. Convective heat transfer to wall (pipe or canister)	Low
12. Convective heat transfer from wall to ambient	Low
13. Radiation heat transfer from wall to ambient	Low
14. Heat of chemical reaction (hydrolysis, oxidation)	High (if applicable)
15. Rate of chemical reaction	Low to High

convective mass transfer from the soil gas to the GAC particle, and conductive heat transfer within a GAC particle are also important mechanisms that define the dynamics of heat transfer within the GAC bed. The heat and rate of exothermic chemical reactions, particularly thermal breakdown reactions, are expected to be significant contributors to temperature rise in the GAC.

A number of mechanisms other than adsorption are considered to be potential significant contributors to the overheating incident. These potential contributors include the effects of flow anomalies in the GAC, presence of trace organics in the soil gas stream, development of "hot spots" in the GAC, particle size distribution of the GAC, and chemical reactions (Appendix E).

Hot spots may occur in the GAC bed for several reasons. Possible reasons include channeling of the gas flow due to uneven bed depth resulting from bed movement or carbon leakage, stagnant bed areas because an accumulation of fines has blocked flow, and the presence of easily oxidized organics such as ketones, aldehydes, or organic acids.

Bench-scale testing has shown that carbon tetrachloride adsorption alone, up to nominal inlet soil gas concentrations of 30,000 ppm, is not sufficient to produce the temperature rise and resultant paint discoloration experienced during the overheating incident. Therefore, one or more of the potential contributors listed above must have occurred to provide the added

heat necessary to raise the temperature high enough to cause the canister exterior paint discoloration.

3.5.3 Bench-Scale Phase I Adsorption Test Results and Analyses

Heat of adsorption calculations based on an isothermal plot for carbon tetrachloride adsorption on GAC revealed that between 118 and 143 Btu of heat is generated per pound of carbon tetrachloride adsorbed. This range brackets the rule-of-thumb estimation of the heat of adsorption, $[1.5 \times 92 \text{ Btu/lb}(\text{heat of vaporization}) = 138 \text{ Btu/lb}]$, stated by several vendors.

Bench-scale adsorption testing also produced an estimate of GAC loading (pound[s] of carbon tetrachloride adsorbed/pound of GAC) as a function of inlet soil gas carbon tetrachloride concentration. Loading increases and heat of adsorption decreases with inlet concentration as shown in Table 3-2. These results are consistent with the finding from the thermogravimetric testing discussed in Section 3.4.2. These counteracting effects result in a roughly linear rate of heat generation with increasing carbon tetrachloride concentration of the inlet flow stream.

3.5.4 Bench-Scale Phase II Adsorption Test Results and Analyses

Temperatures in the GAC column were observed to rise with increased concentrations of carbon tetrachloride in the inlet flow stream as well as other solvents used in each of the tests. For the tests that injected 10,000 ppm_v of carbon tetrachloride into the GAC column, the temperature rises ranged from 80 °F (in Test 1, with 200 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform, and in Test 2, with an increased MEK concentration of 500 ppm_v) to 95 °F (in Test 3, with a MEK concentration of 1,000 ppm_v). With the carbon tetrachloride concentration increased to 40,000 ppm_v (Test 5), the maximum temperature rose about 405 °F. An increase of the carbon tetrachloride concentration to 55,000 ppm_v (Test 6) resulted in a 375 °F temperature rise.

Table 3-2. Adsorption Parameters as a Function of Inlet Carbon Tetrachloride Concentration.

CCl ₄ Concentration (ppm _v)	Calculated GAC loading (lb CCl ₄ /lb GAC)	Heat of adsorption (Btu/lb CCl ₄)	Heat generated at 500 stdft ³ /min (Btu/h)
1,000	0.29	143	1,700
5,000	0.36	134	8,000
10,000	0.42	126	15,100
20,000	0.47	120	28,800
30,000	0.50	118	42,400

CCl₄ = carbon tetrachloride.

GAC = granular activated carbon.

Based on the horizontal array of thermocouples in the bench-scale GAC column set at the depth of 28 in., the temperatures are the highest in the center of the column and decrease toward the external wall of the column. There does not seem to be any significant time delay between the temperature peaks in the center of the column and near the perimeter of the column.

During the tests, a runaway temperature condition was never reached. Tests 5 and 6 (high concentrations of carbon tetrachloride) show that such a runaway condition will not be reached without the presence of other solvents. In particular, MEK hydrolyzes at temperatures below those encountered in the high-concentration tests. Therefore, the presence of MEK in conjunction with high concentrations of carbon tetrachloride would likely produce temperatures requiring the use of a suppression method to keep a runaway condition from occurring.

3.5.5 Possible Events Contributing to Overheating

Chemical reactions may generate enough heat, in addition to the heat of adsorption, to discolor the canister paint. Evidence from the overheating incident that supports at least one type of chemical reaction is the extremely low pH of the water resulting from quenching the overheated canister. It was deduced from this fact that carbon tetrachloride underwent a thermal breakdown and generated hydrochloric acid. The presence of hydrochloric acid was confirmed by the high chloride ion analysis of the quench water.

Additional testing for evidence of hydrolysis was conducted using a laboratory apparatus to load small samples of GAC with carbon tetrachloride at elevated temperatures. One sample was loaded with carbon tetrachloride vapor over a temperature range of 350 to 380 °F. The sample was allowed to cool and then mixed with water. The measured pH of the water was 2.52. This low pH is also indicative of the presence of hydrochloric acid and the hydrolysis reaction.

Other chemical reactions that may have occurred include oxidation of trace organic compounds in the soil gas, oxidation of GAC, and hydrolysis or oxidation of chloroform or methylene chloride, which are known to exist in the soil gas. A possible trace organic compound, MEK, which is occasionally found in the soil gas, is known to oxidize at 210 °F and has been shown to cause hot spots in experimental GAC tests (Appendix B).

All of these reactions are exothermic and could have produced an additional temperature rise in the GAC. Table 3-3 lists several of these reactions and their hypothetical impact on GAC temperature rise. Any of these reactions could have produced a high enough temperature to discolor the canister paint.

Table 3-3. Reaction Heat Release and Relative Temperature Rise.

Reactant ^a	Reaction	Heat of reaction (Btu/lb)	Reactant quantity ^b (lb)	Relative temperature rise ^c	Initiation temperature (°F)
CCl ₄	Hydrolysis	482	0.5	x 4	≥300
CHCl ₃	Hydrolysis	1,350	0.2	x 5	Unknown
CH ₂ Cl ₂	Oxidation	2,260	0.2	x 8	Unknown
MEK	Oxidation	14,600	0.2	x 50	≥212
GAC	Oxidation	14,100	1.0	x 200	≥480
Physical adsorption of CCl ₄	NA	118 ^d	0.5 ^d	x 1	None

^aCCl₄ - carbon tetrachloride, CHCl₃ - chloroform, CH₂Cl₂ - methylene chloride, MEK - methyl ethyl ketone, GAC - granular activated carbon.

^bMaximum quantity of reactant assumed per pound of GAC.

^cThe relative temperature rise is a comparison of the expected temperature increase that would occur from the noted reaction as compared to that produced from adsorbing 0.5 lb of carbon tetrachloride at a concentration of 30,000 ppm_v on to GAC.

^dFrom Table 3-2.

A summary of relevant temperatures obtained from the literature, bench-scale testing, and analytical testing is given in Figure 3-7. The gray band stripe between 550 °F and 660 °F represents the initial and final exterior paint discoloration temperatures. It is concluded that the temperature rise associated with the heat of adsorption of carbon tetrachloride at 28,500 ppm_v was not sufficient to have caused discoloration of the paint. However, the temperature rise is sufficient to have initiated some other type of exothermic chemical reaction, such as determined by laboratory testing.

Heats of reaction added to heat of adsorption may be sufficient to initiate organic compound oxidation, organic compound hydrolysis, or GAC combustion and discolor the canister paint. The reactions have not yet been positively identified. Flow anomalies, rigorous characterization of a representative sample of soil gas, and operating conditions that may generate hot spots have also not been fully investigated. Investigation of these effects will require additional laboratory and bench-scale testing.

3.6 POTENTIAL FOR PHOSGENE GENERATION

An analysis of the potential for generation of phosgene within the GAC-filled canister was performed based on a review of published literature. Additional detail on this analysis is provided in Appendix F. Phosgene is a toxic gas capable of causing severe health effects at very low levels of exposure. At temperatures above 480 °F without catalysts present, carbon tetrachloride can react with water (hydrolyze) to form phosgene. Hydrochloric acid is formed concurrently with phosgene in this reaction. The report

Figure 3-7. Summary of Temperatures Related to Overheating Incident.

probable minimum GAC temperatures achieved in overheating incident

detailed the conditions under which carbon tetrachloride hydrolyzes and the subsequent fate of phosgene.

The conclusions of this analysis are listed below.

- Phosgene was likely to have been generated within the canister at some time during the overheating incident. The phosgene was generated as an intermediate product in the hydrolysis of carbon tetrachloride to form carbon dioxide and hydrochloric acid. The hydrolysis reaction was estimated to occur above 480 °F. It is not possible to estimate the quantities of phosgene generated from the data available.
- Due to the reactivity and kinetics of phosgene with water, it is likely that most of the phosgene was converted to carbon dioxide and hydrochloric acid, especially after the canister was flooded with water.
- Any phosgene that did not react with water was most likely adsorbed in the secondary or tertiary GAC canisters. Any phosgene left unreacted likely adsorbed onto the GAC with a removal efficiency from the soil gas in the same range as demonstrated for carbon tetrachloride.
- It is unlikely that phosgene escaped the VES in concentrations greater than the permissible exposure limit of 0.1 ppm_v either during or after the overheating incident.

3.7 EVALUATION OF CARBON TETRACHLORIDE TREATMENT ALTERNATIVES

An engineering study was performed to evaluate the use of alternative methods to treat extracted soil gas from the 200 West Area Carbon Tetrachloride ERA. The complete results of the study are discussed in detail in Appendix G.

This evaluation is based on the need to determine if there is a more cost-effective process for processing the carbon tetrachloride-laden vapor. The selection of the alternatives to be considered was done under the assumption that each would use the existing GAC units to adsorb carbon tetrachloride from the soil vapor either as the baseline treatment or as a supplement to the alternative technologies. This allows the inclusion of treatment alternatives that alone would not meet the 10 ppm_v requirement. It also provides a backup system for the primary treatment to handle overflow or shutdown of the primary system. Three alternative treatment technologies were selected for consideration and were compared to the current practice of using GAC with offsite reactivation. The three evaluated process alternatives are thermal oxidation, condensation by mechanical refrigeration, and condensation by liquid nitrogen. Each of these treatment alternatives is discussed briefly below.

3.7.1 Existing GAC System

Currently, the exhaust vapor from the VES is directed through a series of GAC-filled canisters to remove the carbon tetrachloride from the vapor

before it is released into the atmosphere. As canisters are loaded to capacity with carbon tetrachloride, they are removed from the system and replaced with fresh canisters. The spent GAC is transported to the reactivation facility in Pennsylvania.

The total cost of the existing system is estimated to be \$5.68 per pound of carbon tetrachloride removed.

3.7.2 Thermal Oxidation

Thermal oxidation is a treatment process in which the carbon tetrachloride in the vapor stream is oxidized at high temperatures into carbon dioxide and hydrochloric acid. The GAC would be used downstream of the thermal oxidation unit as a polishing process, and the hydrochloric acid would be treated by a neutralization process prior to being exhausted.

The total cost of the thermal oxidation system ranges from \$0.76 per pound of carbon tetrachloride removed (decreasing the concentration from 1,000 to 10 ppm_v) to \$3.17 per pound of carbon tetrachloride removed (decreasing the concentration from 30,000 to 300 ppm_v).

3.7.3 Condensation by Mechanical Refrigeration

Mechanical refrigeration would cool the VES exhaust stream in order to condense the carbon tetrachloride (and other soil gases, including water vapor) out of the air flow. Two configurations of the mechanical refrigeration process were considered. A two-stage system would be able to produce a temperature of -40 °F, and a corresponding outlet carbon tetrachloride concentration of 3,000 ppm_v. A similar three-stage system could be used to produce temperatures of -64 °F or -103 °F, with corresponding outlet carbon tetrachloride concentrations of 1,000 and 100 ppm_v, respectively.

The total cost of a mechanical refrigeration system ranges from \$0.81 per pound of carbon tetrachloride removed (decreasing the concentration from 1,000 to 100 ppm_v) with onsite use of the waste to \$2.57 per pound of carbon tetrachloride removed (decreasing the concentration from 10,000 to 3,000 ppm_v) with offsite disposal of the waste. A cost of \$7.32 per pound for the mechanical refrigeration with inlet and outlet carbon tetrachloride concentrations of 1,000 ppm_v (representing an idle refrigeration system) is due to baseline GAC use and expenses incurred by the construction of the refrigeration system.

3.7.4 Condensation by Liquid Nitrogen

Condensation by liquid nitrogen is functionally similar to the mechanical refrigeration alternative. However, the driving force that cools the VES exhaust stream is liquid nitrogen rather than electricity.

The total cost of the liquid nitrogen alternative ranges from \$1.16 per pound of carbon tetrachloride removed (decreasing the concentration from 30,000 to 100 ppm_v) with onsite use of the waste to \$1.72 per pound of carbon tetrachloride removed (decreasing the concentration from 10,000 to 1,000 ppm_v).

with offsite disposal of the waste. A cost of \$8.55 per pound for the refrigeration by liquid nitrogen is derived from an idle refrigeration system, as discussed in Section 3.7.3.

3.7.5 Summary of Evaluated Alternatives

Selection of a preferred treatment alternative was determined to be a function of cost since the three alternatives met all the screening criteria. From the analysis it was determined the most economical treatment alternative is dependent on the concentration of carbon tetrachloride being extracted. It was concluded that a treatment system utilizing condensation by liquid nitrogen is the most cost-effective alternative for VES exhaust carbon tetrachloride concentrations between 10,000 and 30,000 ppm_v. Onsite use of the condensed carbon tetrachloride is considered to be the most cost-effective means of its disposal followed by offsite incineration. For a VES exhaust carbon tetrachloride concentration of 1,000 ppm_v, the thermal oxidation system is the most cost-effective. The treatment cost associated with every alternative treatment system is estimated to be less than that of the baseline system, with the exception of the costs associated with an idle refrigeration system, as discussed above.

4.0 CORRELATIONS OF TASK INVESTIGATION CONCLUSIONS

This chapter focuses on the effects of the overheating incident and the known and possible causes of those effects. It draws together the most relevant information of the task investigations presented in Chapter 3. Supporting evidence is cited to establish the cause and effect relationships. Where appropriate, data gaps are discussed. Chapter 5 lists recommendations for future efforts to address the data gaps and to develop controls to prevent recurrence of overheating.

4.1 CORRELATION OF PAINT DISCOLORATION WITH BENCH-SCALE TESTING

There appears to be a good correlation of results between the paint discoloration test and the observed results from bench-scale testing. These tests contribute greatly to an understanding of the type of reaction that occurred during the June 3 overheating incident.

The paint coupon tests were used to define the maximum temperature achieved in the canister during the overheating incident. This was determined by measuring the temperature needed to achieve a similar paint discoloration on a coupon that was representative of the canister. This test showed that at 550 °F the paint began to discolor to a cocoa-brown shade, at 660 °F the color changed to a dark brown, and above 660 °F the paint began to blister. From this test it is evident that the canister reached a temperature of between 550 to 660 °F.

The bench-scale adsorption tests were used to establish a relationship between peak temperature measured in a GAC-filled column versus inlet concentration of carbon tetrachloride. This testing found the peak thermal wave temperature (Section 3.5.2) to be linearly proportional to the inlet carbon tetrachloride concentration over a nominal range of 1,000 to 30,000 ppm_v. At concentrations between 30,000 and 55,000 ppm_v, the linear temperature relationship is not valid. Data indicate that a maximum or plateau temperature of approximately 480 °F would occur in the column at a concentration of 45,000 ppm_v. At higher concentrations the temperature is not expected to increase above this plateau level as indicated by the Phase II bench-scale testing.

Based on these test results it can be concluded that carbon tetrachloride adsorption cannot be solely responsible for the GAC overheating incident. The best estimate of the carbon tetrachloride concentration during the overheating incident is 28,500 ppm_v. This concentration corresponds to a peak GAC temperature of approximately 250 °F (from the bench-scale testing), which is substantially below the 550 °F experienced in the canister during the overheating incident.

Additional bench-scale testing was performed on the adsorption of carbon tetrachloride mixed with solvents. Three solvents, methylene chloride, MEK, and chloroform, at concentrations ranging between 200 and 1,000 ppm, were mixed with carbon tetrachloride and adsorbed on the GAC column. At 10,000 ppm_v carbon tetrachloride, the presence of these solvents increased the peak GAC temperature from 130 °F to 155 °F.

Because of safety constraints, a carbon tetrachloride mixture in the 30,000 ppm_v range with MEK present was not tested because of the danger of producing phosgene gas. It was concluded, based on an assumed MEK oxidation temperature of 210 °F, that sustained oxidation would occur at this concentration. It is also postulated that once sustained MEK oxidation begins the temperature in the column would rise to a level sufficient to begin the hydrolysis of carbon tetrachloride, which would in turn produce phosgene gas. The combination of the above two reactions is believed to be sufficient to generate a temperature in excess of 550 °F, which would cause paint scorching.

4.2 CORRELATION OF HEAT BALANCE WITH LABORATORY TESTING

A number of significant heat transfer mechanisms were identified as contributing to the temperature rise associated with adsorption of carbon tetrachloride on GAC (Appendix E or Section 3.5.2). A heat balance analysis was calculated using these mechanisms. The analysis was based on adsorbing carbon tetrachloride at a concentration of 35,000 ppm_v. The result of the analysis was compared to the quantity of heat stored in the GAC column (based on measured temperatures) and was found to have excellent agreement. Based on this analysis, it is concluded that the major heat transfer mechanisms for carbon tetrachloride are identified and no significant exothermic reactions are occurring. Extrapolating the results from this analysis to the overheated canister incident cannot be done without time-dependent temperature data and a knowledge of inlet gas composition.

4.3 ADDITIONAL HEAT FROM CHEMICAL REACTIONS

While the heat of adsorption alone is not sufficient to cause the observed scorching, other chemical reactions may have contributed additional heat. Carbon tetrachloride at concentrations somewhat above 30,000 ppm_v may have resulted in sufficient heat through adsorption to have initiate hydrolysis. Other reactions, such as oxidation of organic compounds, may have raised the temperature of GAC loaded with adsorbed carbon tetrachloride sufficiently to initiate a hydrolysis reaction.

Two published papers give initiation temperatures for the oxidation of several organic compounds adsorbed on GAC at levels as low as 210 °F. One of the organic compounds cited was MEK.

Thermogravimetric testing of Envirotrol GAC may have produced a lower hydrolysis temperature than the 480 °F value found in literature. Results from these tests showed that an exothermic reaction involving carbon tetrachloride adsorbed to GAC may begin at temperatures as low as 300 °F. The reaction may be hydrolysis of carbon tetrachloride. Conclusive evidence (low pH) of hydrolysis was found in samples of GAC that had been loaded with carbon tetrachloride and heated to 380 °F.

The pH of the GAC water extract following the bench-scale adsorption tests was basic, indicating that little, if any, hydrolysis had occurred. Thus, the measured peak temperature of 270 °F was apparently too low to initiate this reaction.

Thermogravimetric analysis of the type of GAC used in the overheating incident showed that it begins to slowly oxidize at a temperature of 480 °F. The GAC loaded with adsorbed carbon tetrachloride began to oxidize at 630 °F.

The results of the above analyses indicate that adsorption peak temperatures of 270 °F at 30,000 ppm, are probably high enough to initiate oxidative reactions of adsorbed MEK and similar organic compounds, if present. A temperature of 270 °F is borderline for initiating hydrolysis reactions. Oxidation of the GAC would have been among the last reactions to initiate; however, the discoloration temperatures were high enough to suggest that GAC oxidation may have occurred.

4.4 CHEMICAL ANALYSES OF SOIL GAS

The organic analyses conducted on samples of soil gas obtained from the incident well headspace revealed only part-per-billion-by-volume levels of oxidizable organics including MEK. Concentrations at this level are expected to have little effect on heat generation in a GAC-filled canister. It is not known whether competitive adsorption on the GAC may have concentrated organics and, thus, caused an appreciable local concentration of oxidizable organics. Experts have indicated that an increase of 50% to 100% in concentration has been observed in laboratory adsorption experiments involving flow streams containing two or more adsorbable gases. An appreciable concentration of trace gases in the extracted soil gas could have been a factor in producing the discolored streak on the overheated canister.

Moreover, the samples taken for the analysis may not have been representative of the soil gas treated in the VES at the time of the incident. The sampling occurred at low gas extraction rates, resulting in air samples that were representative of the soil gas near the well's screened intake. The VES, which operates at high gas extraction rates, has a large sphere of influence and probably withdrew soil gas from distances as far as 100 ft from the intake. It is possible that trace contaminant levels were higher within the radius of influence.

A sample obtained at high extraction rates is key to defining the inlet soil gas composition and determining if oxidizable organics exist in appreciable concentrations at the incident site.

4.5 CORRELATION OF BENCH-SCALE TESTING WITH THE OVERHEATING CANISTER INCIDENT

Based on information gained from the paint coupon test, the bench-scale testing and the heat balance analysis, it is concluded that carbon tetrachloride adsorption alone cannot generate the heat required to scorch a GAC-filled canister. It is further concluded that the temperatures required to cause canister scorching, at least 550 °F, could only be achieved through some type of exothermic reaction.

Several factors, resulting from, or consistent with bench-scale test results, have been identified that could have caused or contributed to the generation of the excessive heat.

- Flow anomalies may have occurred in the GAC, restricting convective cooling and creating hot spots of sufficient temperature to initiate hydrolysis of carbon tetrachloride or oxidation of other solvents.
- The very low pH measured in the water taken from the canister following quenching is evidence that a chemical reaction occurred. Analysis of this water also showed high chloride content, which indicates the presence of hydrochloric acid, a product of the hydrolysis of carbon tetrachloride. The quantity of chloride measured indicates that approximately 30% of the carbon tetrachloride was reacted through hydrolysis (some of this may have occurred during the water quenching).
- Hydrolysis of carbon tetrachloride is an exothermic reaction with a reported initiation temperature of 480 °F (uncatalyzed). This temperature is well above the 270 °F measured during bench-scale testing at 30,000 ppm_v carbon tetrachloride. Adsorption alone of carbon tetrachloride appears inadequate for initiating an uncatalyzed hydrolysis reaction.
- Thermogravimetric tests have shown that hydrolysis of adsorbed carbon tetrachloride occurs at temperatures of 380 °F and may occur as low as 300 °F.
- Oxidation of organic compounds such as MEK has been reported at temperatures as low as 210 °F.
- Analysis of soil gas from the ERA site has shown the presence of chloroform, methylene chloride, and MEK at 80, 80, and 149 ppm_v, respectively. Phase II bench-scale testing showed that oxidation of trace solvents contributes additional heat. The testing demonstrated that below 10,000 ppm_v carbon tetrachloride there is not sufficient heat to oxidize the solvents. Testing at higher concentrations of carbon tetrachloride in the presence of other solvents was not performed; however, analysis indicates that adsorption peak temperatures of 270 °F at 30,000 ppm_v carbon tetrachloride are high enough to initiate oxidation.

One possible scenario, consistent with the factors noted above, is that the heat of adsorption at 28,500 ppm_v was sufficient to initiate oxidation of MEK, which in turn generated sufficient heat to initiate hydrolysis of the carbon tetrachloride. *There is insufficient data to postulate such a scenario as anything other than one possible explanation.*

The primary evidence that a chemical reaction occurred in the overheated canister is the observation of the very low pH measured in the water taken from the canister following water quenching. The water was chemically analyzed and determined to have a high chloride ion content. The high chloride levels combined with the low pH indicates the presence of hydrochloric acid. The hydrochloric acid was probably created as a product of the hydrolysis of the adsorbed carbon tetrachloride.

The quantity of chloride measured indicates reaction of 30% of the carbon tetrachloride by hydrolysis, assuming loading at an average of

28,500 ppm_v. Part of the hydrolysis may have occurred when water was added to the overheated canister. The hydrolysis reaction is exothermic; its published, uncatalyzed initiation temperature is 480 °F. This temperature is well above 270 °F peak temperature measured in the bench-scale tests at a nominal concentration of 30,000 ppm_v of carbon tetrachloride. Hence, the effect of adsorption at 28,500 ppm_v appears inadequate for initiating the uncatalyzed hydrolysis reaction.

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5.0 CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the primary conclusions drawn during the course of this investigation and makes recommendations regarding actions to ensure safe startup and operation of the Hanford Site VES.

5.1 CONCLUSIONS OF OVERHEATING INCIDENT STUDIES

Experimental data appear to be more useful than mathematical modeling in determining the causes of the overheating incident and establishing realistic limits for safe operation. Mathematical modeling cannot be used in the near-term to effectively deal with the multiple partial differential equations necessary to represent the complex heat and mass transfer mechanisms that occur during the adsorptive and reactive processes that may occur in a GAC-filled canister. It also cannot be used to predict the impact of flow anomalies in the GAC.

Operations at the estimated 28,500 ppm_v inlet soil gas concentration of carbon tetrachloride measured more than an hour before the incident did not release enough heat by adsorption alone to cause discoloration of the canister paint. This heat did, however, cause a temperature rise sufficient to initiate a chemical reaction(s) as shown by chemical analyses and laboratory testing. The type of chemical reaction that occurred is unknown but is suspected to be caused by oxidation of a solvent and/or hydrolysis of carbon tetrachloride. The heat of this reaction and subsequent chemical reactions, added to the heat generated by adsorption, was sufficient to raise temperatures high enough to discolor the canister paint.

Bench-scale adsorption tests indicate that operations at 1,000 ppm_v inlet soil gas concentration of carbon tetrachloride pose little risk of initiating exothermic chemical reactions. Less than a 5 °F peak temperature rise was measured at this concentration. This temperature was also observed in a second test at 1,000 ppm_v that included MEK at a concentration of 200 ppm_v.

Results of bench-scale testing show it is possible to safely operate at inlet carbon tetrachloride concentrations of 10,000 ppm_v with certain operational controls in place. This conclusion is based on the following observations.

- Peak temperatures measured in bench-scale adsorption tests conducted at a nominal concentration of 10,000 ppm_v carbon tetrachloride were highly stable and did not exceed 155 °F at an inlet temperature of approximately 70 °F.
- No significant evidence of hydrolysis through pH testing was found in samples of GAC exposed to carbon tetrachloride vapor and temperatures as high as 470 °F.
- Oxidation initiation temperatures are reported as low as 210 °F for readily oxidizable organic compounds, including MEK.

- The GAC operating temperature at 10,000 ppm_v will allow for accommodation of both normal variations in carbon tetrachloride concentrations and concentrations of trace organic compounds typical of maximum levels observed in soil gas samples.
- Controls for ensuring safe operations and appropriate corrective responses to offnormal conditions are proven in industrial applications and/or are direct extensions of simple, existing technologies.

Controls that ensure safe operations may include the following.

- A maximum GAC temperature of 150 °F should be considered as a safe operating threshold. Inlet gas temperatures higher than 80 °F may dictate that operations be conducted at lower carbon tetrachloride concentrations in the gas stream to prevent exceeding the threshold temperature.
- The inlet gas stream should be monitored, at a frequency determined by operational experience, for concentrations of carbon tetrachloride, MEK, and other combustible organics that may be present in the soil gas. Ultimately, the process control system would be interlocked with soil gas concentration monitors to avoid exceeding safe concentration thresholds.
- Concentration thresholds have been established for extracted experience, gases to prevent an unacceptable rise in temperature. Concentration thresholds of carbon tetrachloride, MEK, methylene chloride, and chloroform at 10,000, 500, 200, and 500 ppm_v, respectively, are proposed.
- Means of monitoring for signs of exceeding safe thresholds should be provided. The use of a sensitive carbon monoxide/dioxide monitor may provide an early indication of unacceptable rates of oxidation and/or hydrolysis, for example.
- Means of cooling GAC after a period of loading should be provided, if shown to be necessary by further bench-scale testing, e.g., a nitrogen gas purge to remove oxygen and allow for long-term conductive cooling to the ambient air or an auxiliary blower to achieve convective cooling to the air.
- Means of suppressing an overheated condition or conditions believed to be capable of causing an overheating incident should be provided. Examples include cooling with a flow of ambient air, use of a nitrogen gas purge, and water quenching. Each of these examples has limitations on its use, e.g., flowing air will not suppress a significantly overheated condition, nitrogen gas purge will not suppress hydrolysis reactions, and water quenching creates a secondary waste requiring treatment and disposal.

5.2 RECOMMENDATIONS

This section contains recommendations for ensuring a safe restart of the VES through (1) rigorous characterization of the soil gas before and during production operations, (2) establishment of operational thresholds for factors known to affect the temperatures within the canisters, and (3) development and implementation of additional measures.

Factors known to affect the temperatures experienced within the canisters are the VOC inlet concentrations, the airstream flow rate, and the inlet air and GAC temperatures. Recommended operational thresholds are listed below.

- Inlet concentrations should not exceed operational levels of 10,000 ppm_v carbon tetrachloride, 500 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform. If other solvents are detected in the airstream above 10 ppm_v, appropriate concentration thresholds should be established. These levels are based on a maximum gas inlet temperature of 70 °F and a maximum operational flow rate of 500 ft³/min through the canister. If either the inlet gas temperature or the initial GAC temperature rises above 70 °F, it is necessary to operate at either lower volatile organic carbon concentration thresholds or a lower flow rate to prevent the GAC temperatures from exceeding 150 °F.
- The temperature within the canister should not exceed 100 °F at the initiation of operation. If it does, ambient air should be forced through the canister until the temperature falls to 100 °F or lower.

Additional measures that should be considered include the following.

- Instrument the primary canister with an array of centerline thermocouples. These will provide an indication of operating performance and may provide an indication of offnormal conditions, indicating that corrective action is required.
- A heat suppression system should be provided. The most conservative of the proposed methods, and the only one of which any practical experience exists (following the overheating incident), is water-quenching.

Note: If operations at concentrations higher than 10,000 ppm_v carbon tetrachloride are desired, then further actions are recommended.

- *Additional laboratory and/or bench-scale testing should be performed. Conditions that lead to an overheated canister should be tested to evaluate methods of detecting unstable conditions before overheating occurs. Tests at various gas flow rates and concentrations should be conducted to aid in establishing safe operating thresholds when operating at elevated concentrations.*

- *Prewetting the GAC with approximately 0.5 lb water per pound of GAC should also be investigated as a potential technique for lowering the potential for an overheating incident and increasing the capacity of the GAC for adsorption.*
- *Reaction initiation temperatures and heats of reaction for VOCs known or suspected to accompany carbon tetrachloride in the soil gas should be established through laboratory testing. This will provide a basis for determining appropriate operating thresholds.*

6.0 REFERENCE

DOE-RL, 1991, *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume*, DOE/RL-91-32, U.S. Department of Energy, Richland Field Office, Richland, Washington.

In the original explanation of the incident, it was stated that a carbon-oxygen reaction had caused the overheating. The engineer expressed his belief that the GAC was initially ignited, but was not sure that it was burning at the time of the release of GAC particles through the plastic fitting. He also suggested that the carbon-oxygen reaction could occur at temperatures below the ignition temperature of the GAC.

In reference to the Hanford Site overheating incident, the Savannah River engineer expressed his preference for prewetting the GAC if the water can be applied such that no liquid waste is produced. He suggested monitoring completion of the prewetting operation by observing a sharp drop in relative humidity at the GAC canister outlet. He also expressed support for using thermocouples as an experimental tool to measure the internal temperatures of the GAC. He suggested significant dilution of the incoming carbon tetrachloride concentrations. He noted that plans have been prepared to install catalytic oxidation for removal of the bulk of the contaminants from the flow stream at Savannah River Site prior to polishing with GAC.

A.8.0 REVIEW OF VENDOR CONCERNS DURING GAC SERVICE CONTRACT PROCUREMENT PROCESS

On June 7, WHC procurement files were reviewed for any concerns expressed by prospective vendors in the prebid process. The files contained notes from technical discussions that took place on March 4 and 5, 1992. The purpose of this investigation was two-fold. One reason for the investigation is that as part of the analysis of the canister overheating incident, it is necessary to learn about any operational limits or controls that vendors may have mentioned and about which the VES operations team is not aware.

The second reason for the investigation is to look into suggestions that the Carbon Tetrachloride ERA engineering team was made aware of the potential for GAC bed fires and chose not to take any action concerning that potential. The probable source of the information came during the early hours of the GAC overheating incident when one of the GAC technical representatives was contacted about what should be done. The technical representative made statements to the effect that the potential for a GAC bed fire was discussed during the procurement process for the GAC Service Contract. To date, no documentation that directly speaks to the potential of a GAC overheating incident has been found, except for peripheral information noted in the following letters and discussions.

ACRONYMS AND ABBREVIATIONS

CPT	cone penetrometer
DOE	U.S. Department of Energy
ERA	Expedited Response Action
GAC	granular activated carbon
MEK	methyl ethyl ketone
ppm _v	parts per million by volume
VES	vapor extraction system
VOC	volatile organic compounds
WHC	Westinghouse Hanford Company

27. Meyer, O.A. and T.W. Weber, "Nonisothermal Adsorption in Fixed Beds," *AIChE Journal*, Vol. 13, No. 3, pp. 457-465.
28. Milham, R.C., 1968, *High Temperature Properties of Activated Carbon: Part I. Desorption of Iodine, Part II. Standard Method for Ignition Temperature Measurement*, Savannah River Laboratory, E.I. du Pont De Nemours and Co., Aiken, South Carolina.
29. Murphy, J.L. and H.N. Murty, 1986, *Energy Management In a Packaging Gravure Solvent Recovery Operation*, Westvaco Corporation, Covington, Virginia.
30. Naujokas, A.A., "Preventing Carbon Bed Combustion Problems," *Loss Prevention CEP Technical Manual*, Vol. 12, American Institute of Chemical Engineers, New York, New York, pp. 128-141.
31. Naujokas, A.A., 1985, "Spontaneous Combustion of Carbon Beds," *Plant/Operations Progress*, Vol. 4, No. 2, pp. 120-126.
32. Noweir, M.H., E.A. Pfitzer, and T.F. Hatch, 1973, "Thermal Decomposition of Carbon Tetrachloride Vapors at Its Industrial Threshold Limit Concentration," *American Industrial Hygiene Association Journal*, Vol. 34, pp. 25-37.
33. Nwankwo, J.N. and A. Turk, 1975, "Catalytic Oxidation of Vapors Adsorbed on Activated Carbon," *Environmental Science and Technology*, Vol. 9, No. 9, pp. 846-849.
34. Ozil, P. and L. Bonnetain, 1978, "Theoretical Prediction of Temperature Profiles in an Adsorbent Fixed-Bed," *Chemical Engineering Science*, Vol. 33, pp. 1233-1237.
35. Parmele, C.S., W.L. O'Connell, and H.S. Basdekis, 1979, "Vapor-Phase Adsorption Cuts Pollution, Recovers Solvent," *Chemical Engineering*, Vol. 86, pp. 58-70.
36. Ruhl, M.J., 1993, "Recover VOCs Via Adsorption on Activated Carbon," *Chemical Engineering Progress*, Vol. 89, pp. 37-41.
37. Ruthven, D. M., D.R. Garg, and R.M. Crawford, 1975, "The Performance of Molecular Sieve Adsorption Columns: Non-Isothermal Systems," *Chemical Engineering Science*, Vol. 30, pp. 803-810.
38. Smithson, G.R., "Regeneration of Activated Carbon: Thermal, Chemical, Solvent, Vacuum and Miscellaneous Regeneration Techniques," *Carbon Adsorption Handbook*, Ann Arbor Science Publishers, Inc., pp. 879-903.
39. Wilde, K., 1982, "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon," Correspondence, *Environmental Science and Technology*, Vol. 16, No. 10, pp. 731-733.

A brief summary of the pertinent points of each article may be found in Appendix B.

FIGURES:

A-1	Construction Details of GAC Canister	A-7
A-2	Photographs of Overheated Canister	A-10

TABLES:

A-1	Operational History of 1,500 stdft ³ /min VES Unit at the 216-Z-9 Trench	A-2
A-2	Use of GAC Canister EIS GAC 028	A-4

some lower value, but no solvent recovery system was used, the length of the remediation project would be extended proportionately.

A.6.0 REVIEW OF AVAILABLE LITERATURE

Thirty-nine articles have been obtained and contribute to the understanding of the GAC canister overheating incident. These articles are listed below.

1. Adams, R.E., R.D. Ackley, and R.P. Shields, 1983, "Application of Impregnated Charcoals for Removing Radioiodine from Flowing Air at High Relative Humidity," *Proceedings of the Engineering Foundation*, Schloss Elmau, Bavaria, West Germany.
2. ASTM, 1991, "Standard Guide for Gas-Phase Adsorption Testing Activated Carbon," D 5160-91, American Society for Testing and Materials, New York, New York.
3. ASTM, 1992, "Standard Test Method for Determination of the Butane Working Capacity of Activated Carbon," D 5228-92, American Society for Testing and Materials, New York, New York.
4. ASTM, 1992, "Standard Test Method for Determination of Particle Size of Powdered Activated Carbon," D 5158-92, American Society for Testing and Materials, New York, New York.
5. ASTM, 1986, "Standard Test Method for Determination of Iodine Number of Activated Carbon," D 4607-86, American Society for Testing and Materials, New York, New York.
6. ASTM, 1980, "Standard Test Method for pH of Activated Carbon," D 3838-80, (Reapproved 1990), American Society for Testing and Materials, New York, New York.
7. Boden, N., C.F. Cullis, and A. Fish, "Spontaneous Ignition in Carbon Adsorption Beds," *J. Appl. Chem*, Vol. 12, pp. 145-148.
8. Boiston, D.A., 1968, "Acetone Oxidation," *British Chemical Engineering*, Vol. 23, No. 1, pp. 85-88.
9. Bowes, P.C. and A. Cameron, 1971, "Self-Heating and Ignition of Chemically Activated Carbon," *J. Appl. Chem. Biotechnol*, Vol. 21, pp. 244-250.
10. Calgon, 1991, *Carbon Bed Fires*, Calgon Carbon Corporation, San Mateo, California, October 1991.
11. Calgon, *Estimated Heats of Adsorption and Vapors on BPL Activated Carbon*, Calgon Carbon Corporation, Pittsburgh, Pennsylvania.
12. Chi, C.W. and D.T. Wasan, 1970, "Fixed Bed Adsorption Drying", *AIChE Journal*, Vol. 16, pp. 23-31.

Table A-1. Operational History of 1,500 stdft³/min VES
Unit at the 216-Z-9 Trench.

Date (operating)	Daily hours	Total hours	Flow (stdft ³ /min)	PPM* @ CT-1*	PPM CT1 (CT2 or 3)	GAC #1 Loaded (lb)	PPM @ CT-2 or 3	GAC #2 Loaded (lb)	Total Loaded (lb)
3/31/93	2.00	2.00	23.00	1,676.00	1,676.00	1.82	0.00	0.00	1.82
4/1/93	6.50	8.50	55.00	1,346.00	1,346.00	11.35	0.00	0.00	13.16
4/9/93	4.42	12.92	27.70	9,840.00	9,839.27	28.41	0.73	0.00	41.57
4/12/93	3.20	16.12	20.00	5,920.00	5,909.20	8.92	10.80	0.02	50.51
4/13/93	4.67	20.79	20.00	17,559.00	17,549.00	38.65	10.00	0.02	89.18
4/14/93	3.37	16.29	21.50	5,660.00	5,658.55	9.67	1.45	0.00	98.35
4/15/93	3.87	20.16	22.50	10,390.00	10,384.33	21.32	5.67	0.01	120.18
4/16/93	3.75	23.91	23.00	13,860.00	13,853.05	28.17	6.95	0.01	148.37
4/28/93	2.12	26.03	29.00	18,467.00	18,445.20	26.74	21.80	0.03	175.14
4/29/93	1.00	27.03	75.00	8,475.00	8,464.80	14.97	10.20	0.02	190.13
4/30/93	2.20	29.23	75.00	15,950.00	15,927.30	61.97	22.70	0.09	252.19
5/4/93	6.42	35.65	75.00	13,474.00	13,470.00	152.94	4.00	0.05	405.17
5/5/93	7.00	42.65	108.00	20,033.00	19,270.00	343.52	763.00	13.60	762.28
5/10/93	1.47	44.12	121.00	24,367.00	9,001.00	37.75	15,366.00	64.45	864.48
5/11/93	3.25	47.37	170.00	24,300.00	13,398.00	174.55	10,902.00	142.03	1,181.06
5/27/93	1.00	48.37	70.00	77.50	77.50	0.13	0.00	0.00	1,181.19
6/3/93	2.00	50.37	254.00	28,500.00	27,819.00	333.23	681.00	3.16	1,522.58

*PPM = parts per million by volume of carbon tetrachloride.

*CT-1 = inlet flow to primary canister in treatment train. CT-2 = inlet flow to secondary canister in treatment train. CT-3 = inlet flow to tertiary canister in treatment train.

Currently, the polyvinyl chloride outlet hoses on the GAC canisters are rated for a maximum service temperature of 150 °F. This is another limiting factor regarding temperatures in the flow stream. These hoses can be replaced with hoses with a higher temperature rating if necessary.

A.5.8.3 Prewetting of GAC

Opinions on prewetting the GAC are divided. There is some operating experience to draw upon. Prewetting provides water that both adsorbs to the GAC and occupies pore space capillaries. When heat is generated by adsorption of the VOC onto the GAC, the water serves as an effective heat sink due to its high specific heat and heat of vaporization. The capacity for adsorption of VOCs is initially reduced by the adsorbed water; however, the VOCs preferentially adsorb and drive off the water to a great extent. Prewetting may be a difficult undertaking because too much prewetting will cause free water to accumulate below the GAC bed (excess water must be removed), and too little prewetting limits the cooling effect.

Four experts thought that prewetting was a useful control that could be practically employed. One of the four uses prewetting at an operating site and has demonstrated that the saturation can be monitored by sensing the change in relative humidity at the GAC outlet.

One expert expressed his belief that prewetting was not a useful option since some adsorption capacity would be lost and that the cooling effect would be minimal.

To implement the prewetting option at both VES sites, a water supply system would have to be engineered, as no water supply system currently exists.

A.5.8.4 Introduction of Additional Humidity to the Flow Stream

The introduction of additional humidity to the flow stream was mentioned by two of the experts contacted, who had been informed of this option by the GAC canister supplier at another U.S. Department of Energy (DOE) site. The introduction of humidity (assumed to be a mist) into the flow stream would be presumably introduced via a bleed valve and atomizer. The additional humidity would reduce the adsorption capacity, and hence the overall heat released by adsorption would also be reduced. One reference notes that higher temperatures can be observed with the introduction of water vapor in the presence of oxidizable substances.

A.5.8.5 Carbon Monoxide Monitoring

Carbon monoxide and carbon dioxide will be produced when the GAC begins to oxidize. Sensitive monitors are available that detect slight but significant changes in carbon monoxide concentrations between the GAC canister inlet and outlet. However, the initiation of GAC oxidation implies that the temperatures inside the canister have exceeded the point at which carbon tetrachloride can be hydrolyzed to phosgene and hydrochloric acid (482 °F). Also, achieving the ignition temperature of the GAC implies that a water

Table A-2. Use of GAC Canister EFS-GAC-028.

Date of use	Placement in series	Inlet concentration (ppm _v CCl ₄)	Flow (stdft ³ /min)
04/12/93	Secondary	10.8	N/A
04/13/93	Secondary	15.9	N/A
04/14/93	Secondary	2.3	N/A
04/16/93	Secondary	13.6	N/A
04/28/93	Secondary	10.2	212
04/29/93	Secondary	22.7	75
04/30/93	Secondary	From 2,480 to 24,100 in 3 h	202
05/27/93	Primary	22-81 (CPT well)	N/A
06/03/93	Primary	53 (CPT well) 28,500 (W15-82)	N/A 240

pressuring gas in the primary canister. However, it is unlikely that any significant volume of gas was released via this valve because of the tight fit that exists between the blower impeller and its housing. It is probable that any pressure buildup was relieved primarily through the secondary and tertiary GAC canisters and then out the stack to the atmosphere.

After shutdown of the VES was completed, emergency procedures were implemented. The Hanford Fire Department, among other organizations, was notified. After brief discussions about the nature of the overheated canister and its contents, the fire department began to spray the canister from two sides with a water mist to cool it down. Shortly after the spraying operation commenced, a noncontacting infrared thermometer was used to monitor the temperature of the canister in the vicinity of the paint discoloration. This measurement was 240 °F and was the highest temperature recorded at any time during the incident.

After several sprayings, the canister valves were closed and the process hoses were removed from the primary canister placed in plastic bags. The canister was then moved by forklift to the center of the site yard. The upper canister valve was then opened slightly, with a noticeable release of pressure. After about 4 h of spraying the external surface of the canister and taking temperature readings, the canister temperature appeared to stabilize at about 150 °F. The fire department personnel then departed.

Soon after the fire department personnel left the site, the VES technicians sensed that the external temperature of the canister may have been increasing. However, no measurements were made. Concurrently, discussions

four experts suggested minimum superficial velocities in the range of 50 to 100 ft/m as satisfactory.

According to the canister supplier, the maximum permissible design flow is 650 stdft³/min (Attachment A.7). Given the cross-sectional area of the canister, the maximum permissible design flow will be exceeded at a superficial velocity of 52 ft/m.

A.5.6 TYPE AND FORM OF GAC

Two types of GAC are commercially available: coconut-based GAC and coal-based GAC. Coconut-based GAC, as used in the overheating incident, has a lower ignition temperature than coal-based GAC (generally about 570 °F versus 840 °F). Coconut-based GAC has better retentivity for vapor-phase VOCs and thus is more effective as an adsorbent in this application.

Given the assumption of 1,000 ppm_v carbon tetrachloride, two experts felt that the coconut-based GAC was the proper selection. One expert suggested that coal-based GAC would have been the proper selection under the actual conditions, due to its higher ignition temperature. Another expert stated that the GAC supplier for the VES at the Idaho National Engineering Laboratory suggested changing from coal-based GAC to coconut-based GAC to achieve better retention for chloroform.

One expert made mention of the form of the GAC granules. As supplied, the granules are of random shapes. However, processes are available that produce pelletized carbon chips. According to this expert, pelletized GAC is more likely to produce uniform flow through GAC canisters than randomly shaped GAC. Another expert expressed the same opinion on this matter. Opinions were divided on the subject of whether channeling (nonuniform flow) could have occurred through the canister. Thus the value of pelletized GAC is debatable.

A.5.7 POSSIBILITY OF NONUNIFORM FLOW

The possibility of nonuniform flow through the canister introduces internal heating scenarios that may have led to elevated localized temperatures. Three of the experts expressed their beliefs that the canister design and GAC configuration would be unlikely to produce nonuniform flow. Two others suggested that there was definite possibility of channeling and that the burn pattern on the canister surface might be a manifestation of channeling.

A.5.8 ENGINEERING CONTROLS

This section describes various methods of controlling or preventing overheating of GAC when used in the Hanford Site application.

A.5.8.1 Dilution of Carbon Tetrachloride Concentration

As discussed in Section A.5.2, the experts were unanimous that concentrations must be limited. The preferred method of limiting concentrations

20-mesh stainless steel screen supports the GAC bed inside the canister. The specifications for the exterior coating include a dry temperature resistance of 200 °F for both the primer (polyamide epoxy) and the paint (aliphatic polyurethane). The specifications for the interior coating (epoxy phenolic) indicate a dry temperature resistance of 225 °F.

Carbon-steel butterfly valves, with seals and stainless steel shafts, and aluminum quick-connect fittings are installed on both the inlet and the outlet ports of the canister. (Construction details of the canister made from field measurements of project personnel are shown in Figure A-1.) The canisters are manufactured by Aquatec Engineering and Supply, Inc. (Sulphur, Louisiana).

At the time of the incident, the following conditions existed:

Time of extraction operations:	10:22 a.m. - 12:20 p.m., June 3, 1993
Vacuum level at blower:	100 inH ₂ O
Flow through GAC canister:	240 stdft ³ /min
Soil gas temperature at GAC inlet:	About 69 °F
Pressure on outlet side of blower:	10 inH ₂ O
Ambient temperature:	85 °F
Relative humidity @ inlet temp.:	30% (estimated)
Atmospheric pressure:	29.2 inHg
Cloudy/sunny:	Sunny
Wind speed/direction:	5 mi/h, S 60° W (@12:35 p.m.)

The process control system for this VES records many of the operating parameters at 1-min intervals. The VES operational data recorded during the incident are presented as Attachment A.5.

The carbon tetrachloride concentrations entering the primary canister and the concentrations between the primary and secondary canisters are monitored manually by an infrared acoustic spectrophotometer (Brüel and Kjær model 1301) at 1.5-h intervals. This is in accordance with the Safety Assessment Document (WHC 1993). Hence, only one reading of carbon tetrachloride was taken (10:45 a.m.) during the 2-h run. The concentration of carbon tetrachloride at the stack is monitored at 5-min intervals with a sintered-crystal conductivity detector (Odyssey model 2001). The measured concentrations of carbon tetrachloride during the incident are as follows:

Concentration upstream of primary canister:	28,500 ppm _v
Concentration downstream of primary canister:	681 ppm _v
Concentration at the exhaust stack:	less than 1 ppm _v

A.5.1 CAUSE OF OVERHEATING

Three expert consultants believe that the overheating and scorching of paint on the GAC-filled canister were the result of only heat of adsorption due to the high carbon tetrachloride concentration in the soil gas. Two expert consultants believe that the overheating could not have been caused solely by the heat of adsorption, and suggest that a trace, oxidizable compound must have been present to create the additional heat of reaction to ignite the GAC.

Others believe that it is very unlikely, although possible, that the heat of adsorption alone could have produced sufficient heat to have produced the incident.

Several others offered no opinion about the cause of overheating, but strongly suggested characterizing the flow stream in the normal operating configuration to check for the presence of oxidizable VOCs. Oxidizable VOCs include ketones, aldehydes, and organic acids.

All parties involved in the discussions had no prior experience at the high concentrations of carbon tetrachloride encountered in the overheating incident and suggested that the concentrations be greatly reduced. Acceptable concentrations are discussed in subsequent subsections.

Appendix F details the conditions under which carbon tetrachloride decomposes to hydrochloric acid. Since the pH of the canister rinsate after the incident was less than 1, the presence of hydrochloric acid is inferred. Therefore, conditions in the canister at the time of the incident, or during the water dousing, must have been conducive to creation of hydrochloric acid. The only documented carbon tetrachloride reaction that produces hydrochloric acid without the presence of a catalyst occurs at a temperature of 480 °F. Two types of catalysts, light at 2,537 Å or metal oxides/chlorides, were either not present or unlikely to have been present in significant quantities during the incident. Thus a minimum temperature (480 °F) may be inferred in the canister at the time of the incident based on the assumption that the required catalysts were absent.

A.5.2 CARBON TETRACHLORIDE CONCENTRATION LIMITS

The maximum acceptable carbon tetrachloride concentration for safe adsorption onto GAC has received limited study and has not been discussed anywhere in available literature. Among the opinions offered, limits on carbon tetrachloride concentrations in the gas flow stream are based either on operating experience involving other VOCs or on economic considerations in typical industrial applications. The lack of analytical data on the subject stems from the fact that the heat transfer in a GAC-filled canister is very dynamic and complex, and little agreement has been observed between theoretical and experimental data.

As discussed in Section A.8.0, the implied limit of 1,000 ppm_v in the specification for the services contract met with little concern during the prebid discussions. This limit coincides with several opinions voiced after the incident, including those of two of the recognized experts contacted.

The removal efficiency of the primary canister at the time of measurement was 97.6%, $[(28,500 - 681)/28,500] \times 100$. The minimum detection level of carbon tetrachloride with the Odyssey detector in this field application is about 1 ppm_v.

There is an apparent operational discrepancy between the carbon tetrachloride concentrations during the incident and the GAC Service Contract Statement of Work (Attachment A.6). This Statement of Work was provided to the prospective bidders of the GAC Service Contract and was to serve as the basis for their bids. The carbon tetrachloride loading rates are not specified but can be calculated using different combinations of carbon tetrachloride concentrations and flows. The Statement of Work implies a carbon tetrachloride loading rate of 11.8 lb/h based on a nominal carbon tetrachloride concentration of 1,000 ppm_v, or 10.5 lb/h based on a maximum carbon tetrachloride concentration of 885 ppm_v observed during characterization tests at the 216-Z-1A Tile Field, or 20.8 lb/h based on a "production goal" of 500 lb/day of carbon tetrachloride. All three of these rates differ significantly from the calculated rate of loading at the time of the incident, which was 161 lb/h of carbon tetrachloride.

However, it should be noted that in the Recommended Operating Conditions supplied by Envirotrol, Inc. for the canisters (Attachment A.7), there are recommended maximums for flow, temperature, pressure, and humidity, but no recommended maximums for carbon tetrachloride concentration or mass flux.

During some of the earlier operations, the upper limit of inlet concentration was specified at 3,000 ppm_v carbon tetrachloride. This limit was established because of concerns regarding stack emissions and the efficiency of the treatment train, not because of considerations regarding heat generation within the canisters. After operational data were obtained and a tertiary canister was added to the treatment trains, no inlet concentration limits were imposed for operation in the automatic mode.

Previous characterization work involving several of the wells in the area of the 216-Z-9 Trench area indicates sustained carbon tetrachloride concentrations of the same magnitude encountered during the overheating incident. This suggests that elevated carbon tetrachloride concentrations can be routinely expected during operation of the VES in this area. A method of effectively and safely dealing with these concentrations must be developed.

It should be noted that the total mass flux, 161 lb/h, (240 stdft³/min at 28,500 ppm_v carbon tetrachloride) entering the primary canister during the incident was the highest mass flux observed at the Hanford Site to date. However, previous characterization work in the area of the 216-Z-9 Trench has included operation on more than one occasion at high mass flux rates, 51 lb/h, (108 stdft³/min at 20,000 ppm_v carbon tetrachloride) for as long as 7 h without knowingly overheating the GAC. Details of operating data obtained under other flows and concentrations are given in Table A-1 for comparative purposes. These data suggest that operating at a high mass flux rate can be conducted safely if the adsorption and heat generation of carbon tetrachloride and other VOCs present are understood and controlled.

Figure A-2. Photographs of Overheated Canister.

June 3, 1993 Chemical Reaction at 216 Z 98
(photograph property of Hanford Fire Dept.)

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As discussed in Section A.8.0, the implied limit of 1,000 ppm_v in the specification for the services contract met with little concern during the prebid discussions. This limit coincides with several opinions voiced after the incident, including those of two of the recognized experts contacted.

Higher concentration limits proposed by other expert consultants as possibly acceptable were 3,000 ppm_v and 5,000 ppm_v.

A.5.3 PRESENCE AND LIMITATIONS ON OXIDIZABLE SUBSTANCES

There was unanimous consensus among the experts contacted that the flow stream should be fully characterized for the presence of oxidizable substances, including ketones, aldehydes, and organic acids. The literature documents many instances of carbon bed fires ignited by these substances. The most frequently mentioned compound in the literature associated with GAC fires is methyl ethyl ketone (MEK). One of 30 wells sampled at the 216-Z-1A Tile Field contained MEK at about 149 ppm_v. No samples of VES operating flow streams have been characterized for MEK at the 216-Z-9 Trench, although a postincident well sample showed MEK at part per-billion-by-volume levels.

The experts contacted generally agreed on a limiting concentration for ketones of about 100 ppm_v, although one expert gave an upper limit of 500 ppm_v. However, two experts noted that the effects of oxidizable substances may be cumulative.

One expert also discussed the potential for the spontaneous ignition of GAC with or without adsorbed organic materials, under appropriate conditions. Another expert stated that "almost any reaction can take place on a carbon surface."

A.5.4 IGNITION TEMPERATURE OF GAC

The GAC used on this project was derived from coconut based carbon. The ignition temperature of this carbon is about 572 °F according to most of the experts interviewed who offered an opinion on this subject. One expert offered an ignition temperature of 1022 °F.

One expert who has conducted experiments on GAC beds and columns was careful to distinguish between temperature at which accelerated oxidation occurs (390 °F) and an ignition temperature of about 480 °F. This may imply that the appearance of carbon monoxide or carbon dioxide at the bed outlet is an advance warning of incipient ignition.

A.5.5 SUPERFICIAL VELOCITY

The superficial velocity (in feet per minute), which may be calculated as the flow (in standard cubic feet per minute) divided by the cross-section area of the GAC bed (square feet), is an important design parameter that relates directly to the effect of convective cooling provided by the gas flow stream. There is a distinctly divided opinion on an appropriate value for superficial velocity.

At the time of the incident, the superficial velocity was about 20 ft/m. At the full design flow, the superficial velocity is about 40 ft/m.

Two of the experts consulted thought that the 20 ft/m superficial velocity that existed at the time of the incident was satisfactory. However,

four experts suggested minimum superficial velocities in the range of 50 to 100 ft/m as satisfactory.

According to the canister supplier, the maximum permissible design flow is 650 stdft³/min (Attachment A.7). Given the cross-sectional area of the canister, the maximum permissible design flow will be exceeded at a superficial velocity of 52 ft/m.

A.5.6 TYPE AND FORM OF GAC

Two types of GAC are commercially available: coconut-based GAC and coal-based GAC. Coconut-based GAC, as used in the overheating incident, has a lower ignition temperature than coal-based GAC (generally about 570 °F versus 840 °F). Coconut-based GAC has better retentivity for vapor-phase VOCs and thus is more effective as an adsorbent in this application.

Given the assumption of 1,000 ppm carbon tetrachloride, two experts felt that the coconut-based GAC was the proper selection. One expert suggested that coal-based GAC would have been the proper selection under the actual conditions, due to its higher ignition temperature. Another expert stated that the GAC supplier for the VES at the Idaho National Engineering Laboratory suggested changing from coal-based GAC to coconut-based GAC to achieve better retention for chloroform.

One expert made mention of the form of the GAC granules. As supplied, the granules are of random shapes. However, processes are available that produce pelletized carbon chips. According to this expert, pelletized GAC is more likely to produce uniform flow through GAC canisters than randomly shaped GAC. Another expert expressed the same opinion on this matter. Opinions were divided on the subject of whether channeling (nonuniform flow) could have occurred through the canister. Thus the value of pelletized GAC is debatable.

A.5.7 POSSIBILITY OF NONUNIFORM FLOW

The possibility of nonuniform flow through the canister introduces internal heating scenarios that may have led to elevated localized temperatures. Three of the experts expressed their beliefs that the canister design and GAC configuration would be unlikely to produce nonuniform flow. Two others suggested that there was definite possibility of channeling and that the burn pattern on the canister surface might be a manifestation of channeling.

A.5.8 ENGINEERING CONTROLS

This section describes various methods of controlling or preventing overheating of GAC when used in the Hanford Site application.

A.5.8.1 Dilution of Carbon Tetrachloride Concentration

As discussed in Section A.5.2, the experts were unanimous that concentrations must be limited. The preferred method of limiting concentrations

according to each expert is by dilution with ambient air. The use of ambient air for this purpose may increase or decrease both the temperature and the humidity of the flow stream, depending on ambient weather conditions. These variables impact the effectiveness of GAC adsorption and therefore must be considered in any operating scheme. A process control system for automatically and continuously adjusting the carbon tetrachloride concentration to its allowable limit may have to be developed. Currently, the ambient air valve in the VES is controlled manually.

A.5.8.2 Monitoring of Internal GAC Temperatures

Opinions were divided on the value of using thermocouples to monitor and/or control internal GAC canister temperatures. These opinions were based on whether the experts believed that thermocouples can accurately sense an impending temperature excursion and whether the time lag involved in sensing an impending temperature excursion is excessive.

Three experts stated that thermocouples can yield useful information. One of the three suggested the use of two thermocouples and gave a preferred location.

Four of the experts stated that thermocouples would have either no value or limited value because the insulating value of GAC may mask hot spots.

It should be noted that few of the experts had ever employed thermocouples in this type of application or knew of any actual installation of them.

Tests were conducted at the 306 Building in the 300 Area at the Hanford Site on June 22 and June 27 to evaluate the thermal responsiveness of thermocouples in a GAC-filled canister. Air was passed through a GAC-filled canister outfitted with three internal thermocouples, six external surface thermocouples, and thermocouples in the inlet and outlet ports. The results of this test are provided in Appendix D. In summary, the results show that the thermocouples will not sense even a very large temperature difference over a relatively short distance inside the GAC-filled canister, especially if the hot spot develops over a short period of time. Because of the potential for "hot spots" within the GAC bed (as noted by some of the experts), this test indicates that numerous thermocouples would be needed within the GAC bed to enable detection of hot spots.

The use of thermocouples requires a setpoint for interlocking and shutting down the process control system. Several suggestions were given for the setpoint. One expert suggested 200 °F (originally) and later 150 °F; the latter set point would limit desorption and protect the internal epoxy lining on the canister. A second expert suggested setting the limit at about 25 to 30 °F above the inlet process flow temperature; however, the outlet process flow temperature may be significantly affected during startup by seasonal changes in ambient temperatures. A third expert suggested an internal limit of 240 °F. A fourth expert, who has conducted actual laboratory experiments on GAC beds and columns, has measured internal temperature rises of 77 to 86 °F at 10,000 ppm_v of VOC, and expected a rise of about 140 °F at 30,000 ppm_v carbon tetrachloride.

Currently, the polyvinyl chloride outlet hoses on the GAC canisters are rated for a maximum service temperature of 150 °F. This is another limiting factor regarding temperatures in the flow stream. These hoses can be replaced with hoses with a higher temperature rating if necessary.

A.5.8.3 Prewetting of GAC

Opinions on prewetting the GAC are divided. There is some operating experience to draw upon. Prewetting provides water that both adsorbs to the GAC and occupies pore space capillaries. When heat is generated by adsorption of the VOC onto the GAC, the water serves as an effective heat sink due to its high specific heat and heat of vaporization. The capacity for adsorption of VOCs is initially reduced by the adsorbed water; however, the VOCs preferentially adsorb and drive off the water to a great extent. Prewetting may be a difficult undertaking because too much prewetting will cause free water to accumulate below the GAC bed (excess water must be removed), and too little prewetting limits the cooling effect.

Four experts thought that prewetting was a useful control that could be practically employed. One of the four uses prewetting at an operating site and has demonstrated that the saturation can be monitored by sensing the change in relative humidity at the GAC outlet.

One expert expressed his belief that prewetting was not a useful option since some adsorption capacity would be lost and that the cooling effect would be minimal.

To implement the prewetting option at both VES sites, a water supply system would have to be engineered, as no water supply system currently exists.

A.5.8.4 Introduction of Additional Humidity to the Flow Stream

The introduction of additional humidity to the flow stream was mentioned by two of the experts contacted, who had been informed of this option by the GAC canister supplier at another U.S. Department of Energy (DOE) site. The introduction of humidity (assumed to be a mist) into the flow stream would be presumably introduced via a bleed valve and atomizer. The additional humidity would reduce the adsorption capacity, and hence the overall heat released by adsorption would also be reduced. One reference notes that higher temperatures can be observed with the introduction of water vapor in the presence of oxidizable substances.

A.5.8.5 Carbon Monoxide Monitoring

Carbon monoxide and carbon dioxide will be produced when the GAC begins to oxidize. Sensitive monitors are available that detect slight but significant changes in carbon monoxide concentrations between the GAC canister inlet and outlet. However, the initiation of GAC oxidation implies that the temperatures inside the canister have exceeded the point at which carbon tetrachloride can be hydrolyzed to phosgene and hydrochloric acid (482 °F). Also, achieving the ignition temperature of the GAC implies that a water

dousing system or other effective fire suppression system should be in place for extinguishing the oxidation reaction.

Most of the experts believed that a carbon monoxide monitor, in combination with a water dousing system, is a good safety feature in a GAC adsorption system.

One expert suggested that two alarm levels be set, the first to shut off the process flow to allow the GAC canister to cool naturally and the second to introduce the dousing water.

A.5.8.6 Splitting of the Flow Stream

Project personnel have suggested dividing the flow stream among three treatment trains in the VES in an effort to reduce the loading rate into each canister. By using ambient air for dilution, the flow could be increased and the concentrations reduced simultaneously. This would raise the superficial velocity above previous levels while lowering the heat of adsorption.

A.5.8.7 Preadsorptive and Postadsorptive Ambient Air Cooling

Two experts and project personnel have suggested the flow of ambient air through canisters as a preadsorptive procedure during hot weather. This would eliminate the buildup of heat in the canister resulting from solar heating.

Flushing with ambient air after completing adsorption operations would continue to remove heat from the canister at a relatively rapid rate. Otherwise the bed would cool very slowly because of the low thermal conductivity of GAC. One expert suggested that ambient air be run through the system after adsorbing for a minimum of 24 to 48 h. Another expert saw no value to this procedure, since no additional heat is generated from the adsorption process if the flow is stopped. However, using this procedure would quickly lower an abnormally high temperature in a partially loaded GAC bed, and may allow the bed to be used to full capacity without necessitating reduction in flow stream concentrations.

A.5.8.8 Condensing Unit

As a consequence of the overheating incident, the soil gas concentrations at the 216-Z-9 Trench appear to be excessive for direct adsorption undiluted onto GAC. Many of the experts suggested pretreatment for removal of the bulk of the carbon tetrachloride. Removal by condensing the carbon tetrachloride is being studied, and an associated engineering proposal is being drafted based on the operating objectives at the 216-Z-9 Trench. At this time, it appears feasible to reduce the carbon tetrachloride concentration in the flow stream to the range of 1,000 to 3,000 ppm_v by condensation.

Four of the experts contacted suggested that the use of some solvent recovery system would prove to be much more economical than the use of GAC, which would experience very rapid loading rates at the high carbon tetrachloride concentrations encountered. If the concentrations were limited to

some lower value, but no solvent recovery system was used, the length of the remediation project would be extended proportionately.

A.6.0 REVIEW OF AVAILABLE LITERATURE

Thirty-nine articles have been obtained and contribute to the understanding of the GAC canister overheating incident. These articles are listed below.

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A brief summary of the pertinent points of each article may be found in Appendix B.

A.7.0 GAC OVERHEATING INCIDENT AT ANOTHER DOE SITE

Two discussions have been held with an engineer regarding a similar incident of GAC overheating at another DOE site. The incident occurred in the polishing step of an offgas treatment system.

In the spring of 1993, solvent recovery operations were being performed at the DOE Savannah River Site. Operating conditions included a 70 stdft³/min flow of perchloroethylene at about 5,000 ppm_v and trichloroethylene at about 800 ppm_v into GAC-filled canisters. The canisters were 55-gal drums equipped with plastic fittings.

About an hour after resuming operations following shutdown of the system overnight, GAC was discovered discharging from a hole created in a melted plastic fitting. An analysis of the event and consultation with the vendor indicated that the heat of adsorption generated during the previous day's run slowly migrated through the canister and eventually melted the plastic fittings. No convective heat transfer occurred during the night because the air flow was stopped. Upon startup, the flow of air (and hence oxygen) provided additional fuel to the GAC oxidation process.

Operational changes instituted at Savannah River since the incident include adding 2 gal of water to cold canisters before beginning adsorption to act as a heat sink and running air through the system overnight if the system ran during the day. Solvent recovery operations were allowed to resume when the engineer was able to convince his management that he understood the nature of the problem and had incorporated corrective actions to prevent recurrence.

A followup discussion was held with the engineer to discuss details of the incident. The incident had been downgraded from an offnormal occurrence to a nonroutine incident. The downgrading occurred through application of a DOE-mandated procedure, "Special Incident Reporting Instruction Manual." Using this procedure, a committee was established and it determined that the incident had occurred in a research and development environment. The engineer stated his belief that the incident would not have been downgraded if the extraction process had been operating in the same mode as the VES at the Hanford Site.

The engineer reported that discussions with the canister supplier and a private corporation that had experienced a similar overheating incident were the only external sources of information obtained for explaining the incident at the Savannah River Site.

Regarding postincident analysis, the engineer indicated that the GAC was examined only visually and no samples were sent to the supplier for analysis. He said there was no visible evidence of charring. A desorption analysis on the GAC showed only the same compounds as present in the flow stream. The pH of the overheated GAC was about 7.

In the original explanation of the incident, it was stated that a carbon-oxygen reaction had caused the overheating. The engineer expressed his belief that the GAC was initially ignited, but was not sure that it was burning at the time of the release of GAC particles through the plastic fitting. He also suggested that the carbon-oxygen reaction could occur at temperatures below the ignition temperature of the GAC.

In reference to the Hanford Site overheating incident, the Savannah River engineer expressed his preference for pretreating the GAC if the water can be applied such that no liquid waste is produced. He suggested monitoring completion of the pretreating operation by observing a sharp drop in relative humidity at the GAC canister outlet. He also expressed support for using thermocouples as an experimental tool to measure the internal temperatures of the GAC. He suggested significant dilution of the incoming carbon tetrachloride concentrations. He noted that plans have been prepared to install catalytic oxidation for removal of the bulk of the contaminants from the flow stream at Savannah River Site prior to polishing with GAC.

A.8.0 REVIEW OF VENDOR CONCERNS DURING GAC SERVICE CONTRACT PROCUREMENT PROCESS

On June 7, WHC procurement files were reviewed for any concerns expressed by prospective vendors in the prebid process. The files contained notes from technical discussions that took place on March 4 and 5, 1992. The purpose of this investigation was two-fold. One reason for the investigation is that as part of the analysis of the canister overheating incident, it is necessary to learn about any operational limits or controls that vendors may have mentioned and about which the VES operations team is not aware.

The second reason for the investigation is to look into suggestions that the Carbon Tetrachloride ERA engineering team was made aware of the potential for GAC bed fires and chose not to take any action concerning that potential. The probable source of the information came during the early hours of the GAC overheating incident when one of the GAC technical representatives was contacted about what should be done. The technical representative made statements to the effect that the potential for a GAC bed fire was discussed during the procurement process for the GAC Service Contract. To date, no documentation that directly speaks to the potential of a GAC overheating incident has been found, except for peripheral information noted in the following letters and discussions.

Discussion with Interested Vendor

Date: 12 June 93
To: WHC Procurement Specialist
From: Ebasco Environmental
Subject: Synopsis of Prebid Technical Discussion with Vendor on 03/04/92

This synopsis was compiled from texts of transcribed discussions between the WHC technical representative and a prospective vendor for the GAC canister service contract. A request was made by WHC upper-level management for Ebasco personnel to search WHC procurement files for information relating to over-heating phenomena in GAC canisters which had been potentially discussed in the prebid process.

The WHC technical representative discusses the magnitude of the carbon tetrachloride extraction project and how the adsorption process might be optimized. He suggests that optimization can be accomplished by keeping the driving force high, which is done by keeping the inlet concentration high. He states that 1,000 ppm_v appears in all the testing.

The WHC technical representative indicates that the production rate is expected to be 500 lb/day at each of two sites for a total of 1,000 lb/day, and suggests a loading efficiency of about 30%, which is usually expressed as weight of carbon tetrachloride per weight of GAC.

Another WHC representative discusses the fact that 60% loading efficiency can only be achieved under laboratory conditions. Next, the vendor representative discusses some tests that were done to estimate GAC loading. The concentrations of carbon tetrachloride, MEK, and hydrochloric acid are given as 1,012 ppm_v, 163 ppm_v, and 10 ppm_v, respectively. The vendor used the tests to produce isotherms and predicted that the theoretical loading would be from 20% at 10% of the given concentration to 32% at 100% of the given concentration.

The vendor representative describes the loading as appreciable even if the well concentrations begin to fall off. Next, he cites the specification value of 6.1 µg/mL of air (which refers to carbon tetrachloride in the specification), which he converts to 1,012 ppm_v at 100 °F and 950 ppm_v at a different temperature, which he describes as not critical. Next the vendor representative describes the adsorption conditions as less than 50% relative humidity and 100 °F, and states that loading capacity of the GAC (carbon tetrachloride capacity relative to GAC, on a per weight basis) could be 25% of those described if the relative humidity were 90%. Next, the vendor representative states that the loading rate might be up to 40% if only carbon tetrachloride were present. The vendor representative next discusses the impacts of MEK. First, he mentions that it tends to react to oxidize the carbon, and next mentions that 150 ppm should not be a problem. Next, he states that the vendor has to be concerned if pockets of MEK might exist and they might cause a high heat of adsorption or even a bed fire under certain circumstances.

The vendor representative tells the WHC representatives to be aware of the problem, but says that his company does not think it that will be a problem. Next, the vendor representative emphasizes that the effects of ketones can be minimized by keeping the inlet process temperature below

100 °F. The vendor representative then discusses an adsorption isotherm that shows that the effect of temperature on adsorption does not vary much between 77 °F and 100 °F.

During the discussions, the mass of carbon tetrachloride to be loaded per day is considered. The vendor representative says that although 500 lb/day was discussed, he arrives at 800 lb/day of carbon tetrachloride plus 60 lb/day of MEK, and asks for an explanation. The WHC representative gives 1,500 ft³/min at 1,000 ppm, which figures at 800 lb/day of carbon tetrachloride and 60 lb/day of MEK. The WHC representative mentions that 500 lb/day is just a goal, and that they rarely expect to run at 1,500 ft³/min. Next, the vendor representative says that his company will assume a high rate, allowing 500 lb/day to be exceeded. The WHC representative next mentions that the 1,000 ppm is probably a maximum and not an average, and that the vendor can figure on 500 lb/day at each site. The WHC representative then states that 1,500 ft³/min and 1,000 ppm are no problem, and then raises a question as to whether the 500 lb/day will be maintained by keeping the concentration the same and dropping the cubic feet per minute. The other WHC representative then states that the well concentration is something that cannot be controlled. The vendor representative then asks if they intend to recover 500 lb/day at some lower concentration, to which the WHC representative replies that they may recover 1,000 lb/day or 200 lb/day, which is not under their control.

The vendor representative states that the site will vary in flow and concentration, and asks how this will affect the carbon supply. The WHC representative provides an analogy that indicates that the carbon supply should allow for either slow extraction or rapid extraction. The vendor representative indicates that the carbon can handle the concentration variations quite well, and can accommodate a sudden spike without impacting the effluent flow concentrations.

The WHC representative then mentions that 20,000 ppm has been seen, to which the vendor representative indicates "that did get me a little excited." The WHC representative then assures the vendor representative that there will be an interlock to shut down the system in that case. The vendor representative asks if a maximum concentration alarm will be employed, to which the WHC representative replies that he believes it will be set at 1,000 ppm. The vendor representative replies that 2,000 ppm would not be of concern, to which the WHC representative replies that the concentration will be barely over 1,000 ppm.

Discussion with Interested Vendor

Date: 12 June 93
To: WHC Procurement Specialist
From: Ebasco Environmental
Subject: Synopsis of Prebid Technical Discussion with an Interested Vendor
on 03/04/92

This synopsis was compiled from texts of transcribed discussions between the WHC technical representative and a prospective vendor for the GAC canister service contract. A request was made by WHC upper-level management for Ebasco personnel to search WHC procurement files for information relating to over-heating phenomena in GAC canisters which had been potentially discussed in the prebid process.

At the beginning of this discussion, the WHC representative explains that there will be two units, each withdrawing 500 lb of carbon tetrachloride per day, at roughly 1,000 ppm carbon tetrachloride. He explains that the specifications state about 900 ppm but that the concentration is nominally 1,000 ppm. He adds that they hope to optimize production by maintaining a high concentration.

The vendor representative then asks what kind of heat of adsorption has been seen in the trial work so far, to which the WHC representative replies that he does not know and has not seen any comments on the subject relative to the 1,000 ppm. The vendor representative indicates that the 1,000 ppm is a high concentration and that the mass transfer zone can be felt in the canister as it moves. Again, the vendor representative indicates that the 1,000 ppm is a high concentration, but that it probably isn't too drastic as nothing has been yet noticed. The WHC representative verifies that nothing was noticed yet.

The vendor representative indicates that it is important to keep air moving in the system, and suggests not shutting down the blower as a way to avoid a vent fire. Next, the WHC representative mentions that the relative humidity is expected to be 50% or better. The vendor representative asks if the maximum temperature of the soil gas is 100 °F, to which the WHC representative indicates that the temperature is the result of compression of soil gas in the blower. Next, the WHC representative comments that he doesn't remember that temperature effects are caused by the heat of adsorption, but that he intends to check on that because he hasn't thought about it.

The vendor representative then explains that in solvent recovery systems when a unit is shut off after a dayshift of extraction, and if MEK or other compounds are present, the next morning will find that all the paint has burned off the unit and that the unit interior may contain some ashes generated by internal temperatures of 1,500 to 2,000 °F. For this reason, the vendor representative suggests that the blowers be left on in a system.

Discussion with Interested Vendor

In a discussion with the interested vendor, the vendor representative expressed concern about extended service (>1 year) of the GAC canisters if the canister interior surfaces were not coated with epoxy. (Interior surfaces in the GAC canisters used with the site VES are coated with epoxy.) In this discussion, flows and concentrations in the VES operations were not mentioned.

WHC Technical Representative

An initial discussion was held on June 4 between a WHC technical representative who was present at prebid discussions relating to the GAC canister service contract and an Ebasco employee. This discussion was requested by WHC upper-level management for the purpose of gathering information relating to preincident knowledge of GAC overheating. The representative was not aware of any specific discussions with the prospective vendors concerning potential problems with heat in the GAC canisters.

Another discussion was held with the WHC technical representative on June 8. In this discussion, the WHC technical representative mentions that the heat of adsorption was considered to be negligible based on the concentrations at the 216-Z-1A Tile Field. Also, the representative mentions that the heat of adsorption was not considered by any safety group. The representative also states that the early restriction of 3,000 ppm_v carbon tetrachloride in the influent soil gas per the Safety Assessment Document (WHC 19993) was removed as unnecessary since the GAC canisters were achieving higher than expected efficiency, thereby keeping stack emissions to less than 25 ppm_v.

A.9.0 STATUS OF TECHNICAL ANALYSES OF THE INCIDENT

Several tasks have been undertaken in an effort to understand the canister overheating incident, restart the VES under safe operating conditions, and deal with the waste resulting from the incident. Some of the tasks undertaken included the following:

- Computation of the heat balance during the incident
- Sampling and analysis of physical and chemical properties of GAC
- Sampling and detailed characterization of soil gas
- Identification of compounds desorbed from overheated GAC
- Testing canister coupons for corrosion and paint damage due to high temperature
- Investigation of the potential for phosgene creation and its fate during the incident

- Comparison of treatment alternatives for bulk removal of carbon tetrachloride
- Development and testing of a thermocouple tree
- Simulation of the GAC canister on a bench-scale.

A fundamental understanding of the incident and specific engineering controls that can be implemented to allow a safe restart of the VES are expected outcomes of these tasks.

Most of these tasks have been completed and are briefly described in the following paragraphs.

A heat balance was performed to understand the heat generation, storage, removal, and loss within the canister during the overheating incident. This analysis showed that there were uncertainties in the quantities of heat calculated, leading to variations in heat balances. In the case of a flow stream containing 30,000 ppm_v carbon tetrachloride, a heat input in addition to the heat generated by adsorption is required to explain the temperatures experienced during the overheating incident.

The GAC samples from the vicinity of the darkened paint in the overheated canister were retrieved and analyzed for evidence of oxidation. The tested GAC showed no evidence, either physical or chemical, of deterioration due to overheating. Limited ignition of the GAC may have occurred without ostensible signs of charring, however, according to the experts.

Soil gas was sampled from the incident well to determine if oxidizable compounds were present. Although part-per-billion-by-volume levels of oxidizable compounds including MEK were found, the concentrations did not appear to be high enough for generating significant heat in the GAC canister. However, hydrochloric acid was found in one sample, which raised the questions of whether this compound was present during incident operations and if it contributed to the overheating and acidity found in the overheated canister.

The overheated GAC sample was also analyzed for adsorbed gases. The desorbed compounds were similar in composition and concentration to the soil gas that was sampled in the incident well headspace.

The canister coupons were tested for the effects of exposure to high temperature. To achieve the degree of darkening achieved during the overheating incident, the exterior canister paint required exposure to a temperature range of approximately 550 to 660 °F. The interior epoxy coating, when tested at the same temperature, darkened severely and peeled from the canister steel.

An investigation of the potential for phosgene generation and fate during the incident indicated that phosgene was probably generated in an intermediate reaction, followed by a rapid reaction with available water to form carbon dioxide and hydrochloric acid. The possibility of release of phosgene from the VES was deemed remote because of the presence of the two downstream canisters in which phosgene would have been captured, and because the system integrity was not breached during the incident.

Treatment alternatives for soil gas containing high levels of carbon tetrachloride were compared. This comparison showed that both condensation and thermal oxidation of high carbon tetrachloride concentrations in soil gas prior to polishing with GAC would be cost-effective relative to the present process of GAC adsorption.

A thermocouple tree was tested in a full-size GAC-filled canister to evaluate the effectiveness of the method for determining internal temperatures in the GAC bed. This testing showed that large temperature gradients can exist in GAC-filled canisters and that adsorbed water can serve as a significant heat sink.

A bench-scale simulation of the actual canister was constructed and tested at carbon tetrachloride concentrations that ranged from a nominal 1,000 ppm_v to 30,000 ppm_v. These tests provided data on the relationships between carbon tetrachloride concentration, flow, and temperature rise within the GAC column. The tests also included the addition of 200 ppm_v of MEK to flow streams containing 1,000 and 5,000 ppm_v carbon tetrachloride.

The bench-scale testing showed a nearly linear relationship between inlet carbon tetrachloride concentration and peak temperatures in the GAC. At 1,000 ppm_v inlet concentration, the peak temperature rise in the GAC was approximately 5 °F. At nominal 30,000 ppm_v inlet concentration, the temperature rise in the GAC was approximately 200 °F. The addition of 200 ppm_v of MEK had no measurable effects on peak temperature rise in the 1,000 ppm_v carbon tetrachloride case and a 5 °F increase in the 5,000 ppm_v carbon tetrachloride case.

A.10.0 SUMMARY OF POTENTIAL APPLICABLE ENGINEERING CONTROLS

Based on the available literature and discussions with GAC industry technical representatives, the cause of the canister overheating incident is not fully determined. At the time of the incident the greatest mass flux of carbon tetrachloride yet achieved in the VES was flowing into the GAC-filled canister. Other factors may have complicated the incident, such as the possible presence of methane or ketones. Methane is known to exist naturally in some soils and in sanitary landfills. Ketones may have been used for decontamination of gas bulbs or other types of metallic samplers in operations of plants that disposed liquid waste to the ground. It has also been noted in the literature that the potential exists for the spontaneous ignition of GAC with or without adsorbed organic materials, under appropriate conditions (Naujokas 1985).

There is an apparent operational discrepancy between the carbon tetrachloride concentrations during the incident and the GAC Service Contract Statement of Work. The Statement of Work does not provide a definitive carbon tetrachloride loading rate. However, a range between 10.5 lb/h and 20.8 lb/h can be derived from the document using flow and concentration information. This range is much lower than the calculated 161 lb/h of carbon tetrachloride being loading at the time of the incident. The Statement of Work gives the "nominal" concentration of carbon tetrachloride as 1,000 ppm_v and a "highest VOC readings from 30 stream analyses" of about 900 ppm_v carbon tetrachloride.

In the GAC manufacturer's "Recommended Operating Conditions" for the GAC-filled canisters supplied to the project, there are recommended maximums for flow, temperature, pressure, and humidity, but there are no recommended maximums for carbon tetrachloride concentration or mass flux. Furthermore, a review of the vendor concerns documented during the GAC Service Contract procurement process did not reveal any clearly stated warning of this overheating potential. However, peripheral information was provided that suggested its possibility.

Several possible engineering controls that may be utilized to monitor and control the VES operations in the future have been identified.

- Providing methods and controls to limit soil gas inlet carbon tetrachloride concentrations. This could include dilution using ambient air by manual or automatic methods.
- Providing internal GAC thermocouples to determine if temperatures generated by the heat of adsorption as the adsorption front passes each thermocouple are becoming excessive. The thermocouples may be ineffective for detecting hot spots.
- Providing a carbon monoxide/carbon dioxide monitor to detect the onset of significant GAC oxidation. A water dousing system or inert purge gas could be provided to extinguish a GAC combustion that could not be prevented by ambient air dilution.
- Providing prewetting to add a significant heat sink to the GAC bed. The prewetting may be effective for controlling the temperature rise within the GAC bed during adsorption of carbon tetrachloride. It is not known if prewetting will detrimentally effect the efficiency of carbon tetrachloride adsorption.
- Providing increased humidity in the flow stream before it enters the GAC, to serve as a heat sink during adsorption of carbon tetrachloride. This control may impact the loading capacity of the GAC.
- Providing preadsorptive and postadsorptive cooling by passing ambient air through the canisters. Preadsorptive cooling can remove residual heat that arises from solar heating or from previous adsorption operations. Postadsorptive cooling can remove heat from the GAC canister considerably faster than the current method which relies on conductive heat transfer through the GAC to the canister walls.
- Providing pretreatment to reduce concentrations of carbon tetrachloride in the soil gas, leaving the canisters in the role of adsorbing relatively low concentrations. Certain options require handling and disposition of liquid carbon tetrachloride.

A.11.0 REFERENCES

- Naujokas, A. A., 1985, "Spontaneous Combustion of Carbon Beds,"
Plant/Operations Progress, Vol. 4, No. 2, pp. 120-126.
- WHC, 1993, *Safety Assessment for the 200 West Area Expedited Response
Action for Remediation of Carbon Tetrachloride*, WHC-SD-EN-SAD-004,
Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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2 of 6

ATTACHMENT A.1
OCCURRENCE REPORTS
(NOTIFICATION, 10-DAY, AND FINAL REPORTS)

06-03-93 12:40p	Jim Cary	PFP
06-03-93 1:30p	Mike Boyce	ONC
06-03-93 3:00p	Doug Sherwood	EPA
06-03-93 3:00p	Dave Nylander	Ecology
06-03-93 3:00p	Julie Erickson	DOE-RL
06-03-93 3:00p	Roger Freeberg	DOE-RL

13. SUBJECT OR TITLE OF OCCURRENCE:

Overheated Granular Activated Carbon Canister.

14. NATURE OF OCCURRENCE: [18]

15. DESCRIPTION OF OCCURRENCE:

At approximately 12:20pm on June 3, 1993, the operating personnel at the 200 West Area Carbon Tetrachloride (CCl₄) Z-9 Crib Vapor Extraction Site noticed a burning odor and a 1 X 2 foot discoloration on the outside of the primary granular activated carbon (GAC) canister.

16. OPERATING CONDITIONS OF FACILITY AT TIME OF OCCURRENCE:

The vapor extraction equipment was operating at the time of the occurrence. Extraction operations were being conducted for a two hour period on well 299-W15-82 where a flow of 240 cubic feet per minute was achieved and concentrations of CCl₄ were 28,000 to 30,000 parts per million (ppm). The inlet temperature of the airstream to the GAC was measured at 67.5 °F. Operations were being performed within guidelines the supporting document (SD-WHC-EN-TI-010 Rev. 1), operational safety limits (OSLs) and prudent actions, the Hazardous Waste Operations Plan (HWOP), and GAC manufacturer's specifications.

17. ACTIVITY CATEGORY: [3]

18. IMMEDIATE ACTIONS TAKEN AND RESULTS:

Immediately after observing a problem with the GAC canister operating personnel manually shut down the vapor extraction equipment, closed the isolation valve to the well, and then opened the ambient air valve to the system to relieve any pressure build up that could have occurred.

After securing the system, operating personnel implemented emergency procedures. Notifications were made to personnel working in the area to evacuate the Z-9 operations area. Next, the Emergency Dispatch (811) was called and they notified the Hanford Fire Department. Personnel at the other vapor extraction site (216-Z-1A tile field) were notified to shut down operations. Operations personnel notified the emergency coordinator at the Plutonium Finishing Plant. The 200 area Emergency Control Center was also notified. Further notifications to

management, safety organizations, and other personnel were also made at this time.

The Hanford Fire Department arrived at the site by 1236 hours and responded by dousing the overheated GAC canister with water to cool it down. This was repeated several times and the temperature of the canister was monitored. Initial readings of the canister were 239 °F. The temperature stabilized at 150 °F at 1630 hours and the fire department deemed that the problem was alleviated, they exited the site at this time.

Approximately one half hour after the departure of the fire department the temperature of the GAC appeared to have increased, the fire department was asked to return to the site. Based on discussions with a representative of a carbon manufacturer, the only way to extinguish the heat generation was to fill the GAC with water. The fire department then filled the canister with approximately 600 gallons of water. The temperature of the GAC began to slowly decrease, and eventually stabilized to ambient air temperatures. A zone was established around the canister to prevent unauthorized personnel from entering the area. At approximately 1900 hours, operations personnel exited the site.

Status of the operations are that all vapor extraction units remain shut down until the cause of the occurrence is determined and mitigating measures are in place.

END OF NOTIFICATION REPORT

-
19. DIRECT CAUSE: ☐
20. CONTRIBUTING CAUSE(S): ☐
21. ROOT CAUSE: ☐
-

22. DESCRIPTION OF CAUSE:

23. EVALUATION: (By Facility Manager/Designee)

-
24. IS FURTHER EVALUATION REQUIRED? ☐ Yes ☐ No
 IF YES, BEFORE FURTHER OPERATION? ☐ Yes ☐ No
 BY WHOM:
 BY WHEN:
-

25. CORRECTIVE ACTIONS:

TARGET COMPLETION DATE:

COMPLETION DATE:

26. IMPACT ON ENVIRONMENT, SAFETY AND HEALTH:

27. PROGRAMMATIC IMPACT:

28. IMPACT UPON CODES AND STANDARDS:

29. FINAL EVALUATIONS AND LESSONS LEARNED:

30. SIMILAR OCCURRENCE REPORT NUMBERS:

31. DOE FACILITY REPRESENTATIVE INPUT:

32. DOE FACILITY REPRESENTATIVE NAME AND POSITION:

APPROVED BY:

Balance of Plant Facility Manager Signature Approval required for
all 10-Day, 10-Day Update, and Final Reports.

OCCURRENCE REPORT

Facility/Personnel Information

1. OCCURRENCE REPORT NUMBER: RL-WHC-WHC200EM-1993-0028

2. REPORT TYPE AND DATE: DATE TIME

☐ Notification Report June 3, 1993 1740 MTZ
☒ 10-Day Report June 17, 1993 ____ PTZ
☐ Latest 10 Day Update
☐ Final

200 Area/Env. Restoration-Waste Management
 (Name of Facility)

200 West Area Carbon Tetrachloride Expedited Response Action
 (Facility Function Involved)

Hanford Site/Westinghouse Hanford Company
 (Name of Laboratory Site or Organization)

M. R. Adams (Facility Manager/Designee)	81300 (Org. Code)
Manager, Environmental Restoration Engineering (Job Title)	(509) 376-8361 (Phone No.)
M.C. Hagood (Originator)	Mgr. 200 Area Remediation (Title)
200 Area Remediation Section (Organization)	(509) 376-9664 (Phone No.)

3. OCCURRENCE CATEGORY: [0] Off-Normal

4. CONTRACTOR DIVISION OR PROJECT: [RR/ENV]

5. DOE PROGRAM OFFICE: [EM-40]

6. SYSTEM, BLDG., OR EQUIPMENT:	7. UNCI:	8. PLANT AREA
GAC Canister	No	200 West

9. DATE AND TIME DISCOVERED: June 3, 1993 1220 (PTZ)

10. DATE AND TIME CATEGORIZED: June 3, 1993 1410 (PTZ)

11. DOE-HQ NOTIFICATIONS:

12. OTHER NOTIFICATIONS:

06-03-93 1225 (PTZ)	Emergency Dispatch	WHC
06-03-93 1240 (PTZ)	Jim Cary	PFP
06-03-93 1330 (PTZ)	Mike Boyce	WHC/ONC
06-03-93 1500 (PTZ)	Doug Sherwood	EPA
06-03-93 1500 (PTZ)	Dave Nylander	Ecology

13. SUBJECT OR TITLE OF OCCURRENCE:

Overheated Granular Activated Carbon Canister.

14. NATURE OF OCCURRENCE: [11] Operational Occurrence

15. DESCRIPTION OF OCCURRENCE:

At approximately 1220 (PTZ) on June 3, 1993, the operating personnel at the 200 West Area Carbon Tetrachloride (CCl₄) Z-9 Crib Vapor Extraction Site noticed a burning odor and a 1 X 2 foot discoloration on the outside of the primary granular activated carbon (GAC) canister.

16. OPERATING CONDITIONS OF FACILITY AT TIME OF OCCURRENCE:

The vapor extraction equipment was operating at the time of the occurrence.

17. ACTIVITY CATEGORY: [3] Normal Operations

18. IMMEDIATE ACTIONS TAKEN AND RESULTS:

Immediately after observing a problem with the GAC canister operating personnel manually shut down the vapor extraction equipment, closed the isolation valve to the well, and then opened the ambient air valve to the system to relieve any pressure build up that could have occurred.

After securing the system, operating personnel implemented emergency procedures. Notifications were made to personnel working in the area to evacuate the Z-9 operations area. Next, the Emergency Dispatch (811) was called and they notified the Hanford Fire Department. Personnel at the other vapor extraction site (216-Z-1A tile field) were notified to shut down operations. Operations personnel notified the emergency coordinator at the Plutonium Finishing Plant. The 200 area Emergency Control Center was also notified. Further notifications to management, safety organizations, and other personnel were also made at this time.

The Hanford Fire Department arrived at the site by 1236 hours and responded by dousing the overheated GAC canister with water to cool it down. This was repeated several times and the temperature of the canister was monitored. Initial readings of the canister were 239 °F. The temperature stabilized at 150 °F at 1630 hours and the fire department deemed that the problem was alleviated, they exited the site at this time.

Approximately one half hour after the departure of the fire department the temperature of the GAC appeared to have increased, the fire department was asked to return to the site. Based on discussions with a representative of a carbon manufacturer, the only way to extinguish the heat generation was to fill the GAC with water. The fire department then filled the canister with approximately 600 gallons of water. The temperature of the GAC began to slowly decrease, and eventually stabilized to ambient air temperatures. A zone was established around the canister to prevent unauthorized personnel from entering the area. At approximately 1900 hours, operations personnel exited the site.

Status of the operations is that all vapor extraction units remain shut down until the cause of the occurrence is determined and mitigating measures are in place.

Additional notifications were made to Julie Erickson and Roger Freeberg, DOE-RL, 06/03/93, at 1500 hours.

END OF NOTIFICATION REPORT

19. DIRECT CAUSE: TBD

20. CONTRIBUTING CAUSE(S): TBD

21. ROOT CAUSE: []

22. DESCRIPTION OF CAUSE:

A thorough investigation as to the cause of this incident is currently underway. A draft summary report of this incident titled "GAC Canister Overheating Incident" was provided to WHC by Ebasco Services, Inc. on 6/14/93. The report contains a great deal of background information that will be used in the analysis of the cause of the incident. Based upon the information provided in the report, the apparent cause of the GAC canister overheating was a buildup of heat within the canister due to the adsorption heat generated by loading the carbon tetrachloride onto the GAC material. During the time of the occurrence the greatest mass flux of carbon tetrachloride yet achieved at the site was flowing into the GAC canister. Contributing to the heat buildup was inadequate air flow through the canister to carry the heat away. Other contributing effects are being investigated such as the possible presence of methane or ketones adsorbed onto the carbon, which would enhance this heating effect.

23. EVALUATION: (By Facility Manager/Designee)

This occurrence has uncovered a previously unreviewed safety question concerning the loading of GAC canisters with carbon tetrachloride at the concentrations experienced at the time of the incident. A detailed analysis is currently underway to determine the exact cause of the overheating incident. The possibility of resuming operations with the

-vapor extraction systems controlled at previously demonstrated successful operational levels is also currently being evaluated.

24. IS FURTHER EVALUATION REQUIRED? ☒ Yes ☐ No
 IF YES, BEFORE FURTHER OPERATION? ☒ Yes ☐ No
 BY WHOM: WMC Environmental Safety Assessment
 BY WHEN: 6/25/93

25. CORRECTIVE ACTIONS:

Corrective actions will be assigned after the cause analysis is complete. None have been assigned to date.

TARGET COMPLETION DATE: TBD COMPLETION DATE:

26. IMPACT ON ENVIRONMENT, SAFETY AND HEALTH:

Deferred until the next report.

27. PROGRAMMATIC IMPACT:

This occurrence has resulted in a shutdown of vapor extraction operations until an analysis of the cause of the incident has been completed. This is expected to result in a 3 to 5 week delay in Expedited Response Action (ERA) cleanup efforts for the removal of carbon tetrachloride from the soil beneath the 200 West area. The ERA is a Tri-Party negotiated program with relatively high visibility, however, this shutdown of operations represents only a minor impact to a program which is expected to last between 3 and 5 years.

28. IMPACT UPON CODES AND STANDARDS:

No impact has been determined at this time.

29. FINAL EVALUATIONS AND LESSONS LEARNED:

Deferred until the final report.

30. SIMILAR OCCURRENCE REPORT NUMBERS:

A similar occurrence was discovered to have happened at Westinghouse Savannah River on March 4, 1993. Details of the occurrence are provided in attachment 15 of the above referenced Ebasco report.

31. DOE FACILITY REPRESENTATIVE INPUT:

32. DOE FACILITY REPRESENTATIVE NAME AND POSITION:

APPROVED BY:

Balance of Plant Facility Manager Signature Approval required for
all 10-Day, 10-Day Update, and Final Reports.

OCCURRENCE REPORT

Facility/Personnel Information

1. OCCURRENCE REPORT NUMBER: RL-WHC-WHC200EM-1993-0028

2. REPORT TYPE AND DATE:	DATE	TIME
☐ Notification Report	June 3, 1993	1740 MTZ
☐ 10-Day Report	June 17, 1993	PTZ
☐ Latest 10 Day Update	July 17, 1993	PTZ
☒ Final	August 18, 1993	PTZ

200 Area/Environmental Restoration-Waste Management
(Name of Facility)

200 West Area Carbon Tetrachloride Expedited Response Action (ERA)
(Facility Function Involved)

Hanford Site/Westinghouse Hanford Company
(Name of Laboratory Site or Organization)

<u>M. R. Adams</u>	<u>81300</u>
(Facility Manager/Designee)	(Org. Code)

<u>Manager, Environmental Restoration Engineering</u>	<u>(509) 376-8361</u>
(Job Title)	(Phone No.)

<u>M.C. Hagood</u>	<u>Manager, 200 Area Remediation</u>
(Originator)	(Title)

<u>200 Area Remediation Section</u>	<u>(509) 376-9664</u>
(Organization)	(Phone No.)

3. OCCURRENCE CATEGORY: [0] Off-Normal

4. CONTRACTOR DIVISION OR PROJECT: [RR/ENV]

5. DOE PROGRAM OFFICE: [EM-40]

6. SYSTEM, BLDG., OR EQUIPMENT:	7. UNCI:	8. PLANT AREA
Granular Activated Carbon Canister	No	200 West

9. DATE AND TIME DISCOVERED: June 3, 1993 1220 (PTZ)

10. DATE AND TIME CATEGORIZED: June 3, 1993 1410 (PTZ)

11. DOE-HQ NOTIFICATIONS: See section 18.

12. OTHER NOTIFICATIONS:

06-03-93 1225 (PTZ)	Emergency Dispatch	WHC
06-03-93 1240 (PTZ)	Jim Cary	PFP
06-03-93 1330 (PTZ)	Mike Boyce	WHC/ONC
06-03-93 1500 (PTZ)	Doug Sherwood	EPA
06-03-93 1500 (PTZ)	Dave Nylander	Ecology

13. SUBJECT OR TITLE OF OCCURRENCE:

Overheated Granular Activated Carbon Canister.

14. NATURE OF OCCURRENCE: [11] Operational Occurrence

15. DESCRIPTION OF OCCURRENCE:

At approximately 1220 (PTZ) on June 3, 1993, the operating personnel at the 200 West Area Carbon Tetrachloride (CCl₄) 216-Z-9 Crib Vapor Extraction Site noticed a burning odor and a 1 X 2 foot discoloration on the outside of the primary granular activated carbon (GAC) canister.

16. OPERATING CONDITIONS OF FACILITY AT TIME OF OCCURRENCE:

The vapor extraction equipment was operating at the time of this off-normal occurrence.

17. ACTIVITY CATEGORY: [3] Normal Operations

18. IMMEDIATE ACTIONS TAKEN AND RESULTS:

Immediately after observing a problem with the GAC canister, operating personnel manually shut down the vapor extraction equipment, closed the isolation valve to the well, and then opened the ambient air valve to the system to relieve any pressure buildup that could have occurred.

After securing the system, operating personnel implemented emergency procedures. Notifications were made to personnel working in the area to evacuate the 216-Z-9 operations area. Next, the Emergency Dispatch (811) was called and they notified the Hanford Fire Department. Personnel at the other vapor extraction site (216-Z-1A/-Z-18 site) were notified to shut down operations. Operations personnel notified the emergency coordinator at the Plutonium Finishing Plant. The 200 area Emergency Control Center was also notified. Further notifications to management, safety organizations, and other personnel were also made at this time.

The Hanford Fire Department arrived at the site by 1236 hours and responded by dousing the overheated GAC canister with water to cool it down. This was repeated several times and the temperature of the canister was monitored. Initial readings of the canister after dousing were 239 °F. The temperature stabilized at 150 °F at 1630 hours and the fire department deemed that the problem was alleviated. They exited the site at this time.

Approximately one half hour after the departure of the fire department the temperature of the GAC appeared to have increased, and the fire department was asked to return to the site. Based on discussions with a representative of a carbon manufacturer, the only way to extinguish the heat generation was to fill the GAC with water. The fire department then filled the canister with approximately 600 gallons of water. The temperature of the GAC began to slowly decrease, and eventually stabilized to ambient air temperatures. A zone was established around the canister to prevent unauthorized personnel from entering the area. At approximately 1900 hours, operations personnel exited the site.

Status of the operations is that all vapor extraction units remain shut down until the cause of this off-normal occurrence is determined and mitigating measures are in place.

Additional notifications were made to Julie Erickson and Roger Freeberg, DOE-RL, 06/03/93, at 1500 hours.

END OF NOTIFICATION REPORT

19. DIRECT CAUSE: [4A]

20. CONTRIBUTING CAUSE(S): [4B, 5C, 6A]

21. ROOT CAUSE: [3D]

22. DESCRIPTION OF CAUSE:

The ERA project team has compiled three reports, "Draft Summary Background Report: GAC Canister Overheating Incident", "Draft Summary Analysis Report: GAC Canister Overheating Incident", and "Draft References: GAC Canister Overheating Incident." These reports provide information and analyses on the events surrounding the GAC canister overheating and the cause of the incident. Based on the conclusions presented in these reports, the apparent direct cause of the GAC overheating incident was the rate at which carbon tetrachloride was being adsorbed onto the GAC without adequate heat transfer at the time of the incident, approximately 28,500 parts per million (ppm) at 240 cubic feet per minute (cfm) air flow. Inadequate man-machine interface was interpreted as the direct cause code since the technician was not aware that overheating a GAC could occur, and the machine as engineered provided no warning of the GAC overheating. The root cause analysis findings agree with this conclusion.

The root cause of the off-normal occurrence was determined to be that process knowledge was ineffectively communicated, i.e. personnel who had process knowledge on the effects of heat of adsorption on carbon did not transmit this information to people responsible for managing, designing, reviewing and operating the vapor extraction systems (VES). In addition, organizations with personnel who had knowledge of heat of adsorption did not participate in appropriate VES associated review activities. A "strong" contributing cause cited in the root cause analysis report was the pressure of meeting production milestones. The report emphasized that adequate technical review should not be sacrificed in the name of expedience.

Contributing causes to the incident were determined to be inadequate design, inadequate training, and inadequate administrative control. Inadequate design was cited due to the inability of the GAC canister to handle high concentrations of the contaminant that were known to have existed at the 216-Z-9 site during the GAC procurement process. Inadequate training was cited because technicians did not have the knowledge that heat generation could be a problem with the operation of GAC treatment systems. Inadequate administrative control (management) was cited due to the deficiencies noted of management in insuring that important technical information (i.e. safety considerations of GAC treatment systems) was broadly, completely, and timely disseminated.

The root cause analysis report (Revision 2) that was completed on July 20, 1993 as a result of this off-normal occurrence is provided as an attachment.

23. EVALUATION: (By Facility Manager/Designee)

This off-normal occurrence has uncovered a previously unreviewed safety concern regarding the operation of the GAC treatment system utilized at the CCl₄ ERA site. Knowledge of this safety concern was understood by project personnel, but was ineffectively communicated to people responsible for managing, designing, reviewing and operating the vapor extraction systems. A reorganization of the project team was completed and the team has demonstrated excellent communications and teamwork during the off-normal occurrence and subsequent restart efforts.

A thorough analysis of the direct cause of the incident has been completed. The analysis includes an evaluation of potential engineering solutions that may be implemented to lessen the potential for reoccurrence of another GAC overheating. Furthermore, the worst case consequence of the GAC overheating incident, determined to be the creation and release of phosgene gas, was analyzed. Results of the analysis conclude that exposure of site workers to phosgene gas is highly improbable and therefore does not pose a health risk should another GAC overheating incident occur.

At this time, sufficient information has been gathered and corrective actions initiated to allow the restart of the VES at the 216-Z-1A/-Z-18 site. Operations at this site will be used for further field testing of engineering solutions that may be implemented for the restart of the remaining vapor extraction units at the 216-Z-9 crib. Some of the engineering solutions

A-6000-576 (03/93) GEF040

proposed are alternate/additional treatment systems to remove/reduce the high concentrations of carbon tetrachloride present at the 216-Z-9 site. Implementation of these types of engineering solutions and any others deemed necessary may present additional delays to achieving prior-to-the-occurrence removal capacities, due to engineering, procurement, and installation activities that would be required. These delays, however, are not foreseen to significantly impact cleanup of the 200 west area carbon tetrachloride site, which is expected to be a three to five year program.

24. IS FURTHER EVALUATION REQUIRED? ☐ Yes ☒ No
 IF YES, BEFORE FURTHER OPERATION? ☐ Yes ☐ No
 BY WHOM:
 BY WHEN:

25. CORRECTIVE ACTIONS:

Based on recommendations from the root cause analysis final report, Environmental Restoration Safety, and the project engineering team the following corrective actions have been determined.

1) Develop a justification proposal for restart of vapor extraction at the 216-Z-1A/-Z-18 site. The proposal will provide the basis for resuming vapor extraction at this site and describe the planned operating strategy. The proposal will also describe implementation of each of the recommendations outlined in the root cause analysis final report.

Action: Environmental Restoration Engineering.

2) Implement recommendations of the root cause analysis final report.

Action: Environmental Restoration Engineering.

3) Resolve item number 8 of the root cause analysis final report by providing a follow-up letter to Restoration and Remediation Division management that addresses the likelihood of phosgene exposure to the worker involved in the June 3 off-normal occurrence.

Action: Environmental Restoration/Construction Safety.

4) Revise the safety assessment document (WHC-SD-EN-SAD-004) to address heat of adsorption concerns with operating GAC canisters and provide operational safety limits for operating the VES at the 216-Z-1A/-Z-18 site.

Action: Environmental Restoration Safety Support.

5) Revise Design, Operations, and Monitoring document (WHC-SD-EN-TI-010) to address heat concerns with operating GAC canisters and provide document control methodology for implementing working level procedures for operating the Vapor Extraction Systems at the ERA sites.

Action: Environmental Restoration Engineering.

6) Develop and implement working level procedures that will monitor and control the inlet concentrations of CCl₄ below 1,000 ppm and address proper actions to be taken if another GAC overheating incident occurs.

Action: Environmental Restoration Engineering.

7) Engineer and implement thermocouple controls at the primary GAC canister to monitor inlet and outlet air temperatures for a 20°F differential.

Action: Environmental Restoration Engineering.

8) Complete and obtain concurrences for checklist of readiness review activities prior to restart of vapor extraction operations at the 216-Z-1A/-Z-18 site.

Action: Environmental Field Services.

9) Continue to study GAC adsorption for empirical data that will provide a basis for development of operational safety limits at the 216-Z-9 site.

Action: Environmental Restoration Engineering.

TARGET COMPLETION DATE: October 1, 1993

COMPLETION DATE:

26. IMPACT ON ENVIRONMENT, SAFETY AND HEALTH:

There are no known impacts to the environment, safety, or health as a result of this off-normal occurrence.

27. PROGRAMMATIC IMPACT:

This off-normal occurrence has resulted in a three month delay in ERA cleanup efforts for the removal of carbon tetrachloride from the soil beneath the 200 West area. The ERA is a Tri-Party negotiated program with relatively high visibility, however, this shutdown of operations represents a relatively minor impact to a program which is expected to last between three and five years. Corrective actions to be addressed as a consequence of this off-normal occurrence may delay achieving prior-to-the-occurrence removal capacities, but this is not anticipated to significantly impact the goals of the overall ERA program.

28. IMPACT UPON CODES AND STANDARDS:

There have been no impacts upon codes and standards as a result of this off-normal occurrence.

29. FINAL EVALUATIONS AND LESSONS LEARNED:

There have been many lessons learned as a result of the GAC overheating incident that pertain to both administrative and technical aspects of the 200 West Area Carbon Tetrachloride ERA. Those determined to be most important are described below:

1) GAC Treatment Systems - The project team learned about the heat of adsorption that occurs within GAC treatment systems. Heat is generated on GAC as contaminants are stripped from the passing airstream. Depending on the flux of contaminants entering the canister and/or the presence of other oxidizable substances in the vapor stream, the heat generated due to adsorption can build up within the canister. The primary methods for preventing this occurrence are to control the concentration and flow rate of contaminants being sent to the GAC inlet, and to monitor for the presence of ketones and other easily oxidizable compounds. Other methods for controlling heat buildup within a canister include: 1) prewetting GAC, 2) thermocouple monitoring of GAC bed, 3) addition of humidity to airstream, 4) carbon monoxide monitoring to detect combustion of GAC, 5) pretreatment (e.g. condenser) to remove bulk of contaminant prior to GAC treatment, and 6) alternate treatment (e.g. catalytic or thermal oxidation).

During its investigation, the project team discovered a lack of information in industry about the use of GAC treatment systems, especially as applied to the adsorption of volatile organic compounds in a vapor extraction process. Activated carbon is commonly used in industry, however, most applications specify a nominal concentration of contaminants at a nominal flow. In the process of soil vapor extraction these parameters change with time.

During the project team's attempts to quantify the amount of contaminant that can safely be adsorbed on GAC it was discovered that there is a serious lack of engineering data concerning the heat transfer within GAC treatment systems. Furthermore, "rules of thumb" are generally the standard in the industry for designing GAC treatment containers that will dissipate the heat buildup at a given airflow. It is clear that greater knowledge of GAC adsorption is needed to determine safe operating limits that will insure that the reoccurrence of another GAC overheating incident can be minimized at Hanford. Much of the information needed can be obtained through empirical observations made during continued soil vapor extraction operations and bench scale testing.

2) Oxidizable Substances - The project team learned that oxidizable substances, even at low concentrations, can be a concern for generating excessive heat during operation of GAC treatment systems. Based on this information it is clear that it is important to conduct thorough characterization analyses for oxidizable contaminants within the soil vapor prior to full scale extraction. During full scale extraction, however, entrainment of additional contaminants over time presents an unpredictable factor in vapor extraction operations. To guard against this unpredictability, periodic characterization analyses should be conducted to monitor for entrainment of new contaminants.

3) Decomposition of Carbon Tetrachloride - The project team learned that a GAC overheating incident can produce the necessary conditions for the decomposition of carbon tetrachloride into phosgene and hydrochloric acid. This presents a new safety concern that has subsequently been analyzed for its potential impact to the site worker. Results of the analysis indicate that during a GAC overheating incident any phosgene produced would immediately hydrolyze in the presence of water to hydrochloric acid. Since the vapor stream is typically above 50% relative humidity, a substantial inventory potentially exists for the release of hydrochloric acid vapors. This amount poses a low hazard to site workers, but requires personnel to evacuate the site or don appropriate personal protective equipment during the occurrence of an GAC overheating incident.

4) Process Knowledge - The project team learned the importance of having or obtaining adequate process knowledge of any treatment system that is utilized or being considered for application to a remedial action. This includes thorough understanding the subtleties of both physical and chemical aspects that affect the usage of the treatment.

5) Effective Communications - The project team learned that it is absolutely essential to have effective communications. Engineering of the VES and GAC treatment system is only part of the whole process of soil vapor extraction. Implementing soil vapor extraction requires knowledge from several different fields including geology, hydrogeology, chemical engineering, mechanical engineering, and electrical and instrumentation engineering. It is essential that personnel representing their particular expertise provide input to the project and that their input is taken into account.

6) Knowledgeable technicians - The project team learned the value of having trained, knowledgeable technicians operating the soil vapor extraction equipment. During the GAC overheating event technicians at the site took appropriate action based on their intimate knowledge of how the process operated. Even though the operation is exiting the experimental mode and entering a large scale production mode, it is essential to keep knowledgeable personnel operating the equipment. The GAC overheating incident emphasizes the fact that soil vapor extraction technology is a non-routine operation.

7) Complacency - The project team learned the lesson of becoming complacent in their work. Complacency with operations at the 216-Z-1A/-Z-18 site led to the idea that moving to a new site (216-Z-9) would not present much concern. The team learned that it is essential to examine the impact of any changes that are undertaken with the project whether they are with regard to design, operation, or project management.

The project team also came to the realization that even with apparently benign operations, such as soil vapor extraction, the potential for risk always exists. Furthermore, no matter how much forethought is done to make an operation safe, the potential for risk still exists. Personnel responsible for operating, designing, reviewing, and managing need to be aware of the presence of risk, and exercise care in not becoming complacent when operations are going smoothly.

30. SIMILAR OCCURRENCE REPORT NUMBERS: None

31. DOE FACILITY REPRESENTATIVE INPUT:

32. DOE FACILITY REPRESENTATIVE NAME AND POSITION:

APPROVED BY: M. R. Adams 11/11/93 8/10/93
Balance of Plant Facility Manager Signature Approval required for
all 10-Day, 10-Day Update, and Final Reports.

ATTACHMENT

REV. 2 ROOT CAUSE REPORT FOR THE VAPOR EXTRACTION SYSTEM
OFF NORMAL OCCURRENCE

BACKGROUND

This root cause analysis addresses the circumstances that caused the Off Normal Occurrence at the 216-Z-9 (Z9) trench Vapor Extraction System in the Hanford 200 West area on June 3, 1993 at approximately 12:20 p.m. The Off Normal Occurrence report describes that operating personnel at the 200 West area Carbon Tetrachloride (CCl₄) Z9 trench Vapor Extraction Site noticed a burning odor and a 1 X 2 foot discoloration on the outside of the primary (first of three in series) granular activated carbon (GAC) canisters.

The vapor extraction equipment was operating at the time of the occurrence. Extraction operations were being conducted for a two hour period on well 299-W15-82 where a flow of 240 cubic feet per minute was achieved and concentrations of CCl₄ were 28,000 to 30,000 parts per million (ppm). The inlet temperature of the air stream to the GAC was measured at 67.5 degrees F. Operations were being performed using guidelines of the supporting document WHC-SD-EN-TI-010 Revision 1, operational safety limits (OSLs) and prudent actions, the Hazardous Waste Operations Plan (HWOP), and GAC manufacturer's specifications. It is noted that an OSL limit calculation was based on 25,000 ppm, but the unit was being operated at 28,000 to 30,000 ppm, but the calculation limit was not perceived by the operators as a "de-facto" limit.

When the problem was identified, the operator immediately shut down the entire system, followed emergency procedures which included dialing 811, the fire department responded, and prescribed notifications were made. Details of the occurrence may be obtained from the Off Normal Occurrence Report and subsequent documentation summarizing technical and safety aspects of the occurrence.

Both the Occurrence Reporting process and the PPG value for this occurrence of 31 require that a Root Cause Analysis be performed.

RATIONALE AND APPROACH

Preliminary assessment of conditions and facts relative to the occurrence initially indicated that a root cause determination using Change Analysis might be appropriate. However, as information became more plentiful and accurate it was decided that a root cause determination using Barrier Analysis was more appropriate recognizing the apparent probable contributing factors associated with the occurrence conditions.

The Root Cause Analysis team consisted of DW Brown (Environmental Field Services), RL Hand (Restoration & Remediation Quality Assurance), DO Hess (Safety), RS Pavlina (Liquid Effluent Process Engineering) and RG Dieffenbacher (Environmental Restoration Engineering - team lead). Mr. Pavlina, a chemical engineer, provided the team with an element of independence in that his normal work area is not within or providing direct support to the Environmental Restoration Division, and he has relevant experience with use of activated carbon. Four of the five team members have completed the five day Root Cause course. The Department of Energy observed

the process with their representative Mr. MD Mahoney of the US Army Corp of Engineers. Mr. Mahoney attended all team interviews and meetings.

The team interviewed 16 persons. The interviewees represented Vapor Extraction System (VES) operators, site safety officer, participating engineers, design contributing consulting engineers, procurement, safety analysis, occupational safety, project leads and management.

The team reviewed design documents, procurement specifications, technical literature related to carbon and heat of adsorption, safety analysis documents, procedures, VES daily log entries, and various documents addressing technical conditions related to the occurrence.

The results of the Barrier Analysis addressing the Target, Control of Excess Heat Production - Z9 Vapor Extraction System, are summarized in attachment 1.

CONCLUSION

The root cause of the VES off normal occurrence is that process knowledge was not effectively communicated.

The people responsible for managing, design, review and operation of the process did not have adequate process knowledge of the characteristics of carbon adsorption due to inadequate communication by personnel who had that process knowledge. Knowledge of the effects of heat of adsorption on carbon was not known among VES operating and most support personnel. Organizations that reviewed design, operating and safety documents had personnel that were knowledgeable of heat of adsorption on carbon but were not participants in VES associated review activities. Additionally the VES units operating at the 216-Z-1A (Z1A) site had operated successfully, although at low production levels. Z1A experience tended to generate an atmosphere that Z9 would be equally successful with the ability to substantially increase production not only from an equipment capability perspective, but with the increased concentrations of carbon tetrachloride known to be present in the Z9 area. A main operational concern was to avoid an operating condition that could yield an exhaust stack emission in excess of 25 ppm carbon tetrachloride.

The lack of process knowledge combined with milestones that emphasized production were strong contributors to this incident. There is the possibility that these same contributing factors may carry over on future expedited response actions, treatability studies, and similar activities requiring equipment with inherent, and perhaps subtle aspects, that could lead to adverse circumstances. Caution should be exercised that forces such as milestones, customer, and/or regulator pressures not create an environment where "the details" are given lower priorities. Adequate technical review should not be sacrificed in the name of expedience.

It was noted by the Root Cause Analysis team during the course of its activities, that there appeared to be low possibility of a similar occurrence at the Z1A VES operation. The primary reason for this is because of the very low concentrations of carbon tetrachloride being experienced at the Z1A site. Although concentration levels at Z1A should continue to be monitored no reason to discontinue, postpone, or alter equipment or operating methodology was

envisioned, unless the carbon tetrachloride concentrations increase inordinately.

The alertness of the operators in detecting the situation, and their response to it, was found to be commendable. The prompt detection and action averted what could have evolved into a more serious situation.

RECOMMENDATIONS

The Root Cause Analysis team makes the following recommendations based on the team's analysis and observations made during the course of their effort. There is no prioritization applied to the following list.

1. Design considerations:

- o Provide monitoring such as carbon bed temperature and/or GAC outlet carbon dioxide and/or carbon monoxide. Consideration should be given to coupling sensors to equipment shut down or other means of limitations to preclude adverse conditions from occurring.

2. VES Operation considerations:

- o Characterize inlet vapors for potentially adverse hydrocarbons including ketones and aldehydes along with CCl_4
- o Limit GAC inlet feed concentrations of CCl_4 and other contaminants based on heat loading calculations for the GAC canisters. This will limit heat generation problems and the potential for creating harmful byproducts.

3. Verification considerations:

- o Establish methodology for field verification that GACs are what were ordered.
- o Take carbon grab samples from randomly selected newly received GACs for analysis.

4. Management considerations:

- o Management should assure that persons with appropriate technical expertise are involved in the design and persons with appropriate technical expertise, experience and operations personnel are included as design reviewers.
- o Management needs to be especially sensitive that technical information is broadly, completely, and timely disseminated to appropriate personnel.
- o Management should be more sensitive to staff inputs relative to operating limits and other factors before making schedule and production commitments. Consideration should be given to requesting schedule commitment change.

5. Procedure consideration:

- o Investigate separating the operating procedure from the design oriented portion in WHC-SD-EN-TI-010 Design, Operations, and Monitoring of the Vapor Extraction System at the 216-Z-1A Tile Field.
- o Consider using separate procedures for VES units of different capacities i.e. 500 cfm and 1500 cfm. It was noted that ECN 196005 added operation and other changes to existing Z1A oriented instructions to facilitate Z9 oriented activities.
- o Operating instructions should be included for controlling heat of adsorption in all operating modes i.e. automatic and manual.
- o Emergency response should address internal overheating and fire possibility. Specific procedural processes should prescribe means for cooling overheated GACs rather than a total power shutdown, although that action was most appropriate under the circumstances as understood by the operator at the time of the occurrence.
- o Procedures should include operating limits for inlet concentration/charcoal load rate.
- o Design and analytical limitations should be addressed and integrated into procedures, safety assessments, HWOP, etc.

6. Safety considerations:

- o Safety documentation should be amended to reflect the heat of adsorption and possible internally generated fire hazards of charcoal operation.
- o OSLs should include operating limits for inlet concentration/charcoal loading rate.

7. Training considerations:

- o "Classroom" train all personnel in the operation of charcoal and of primary safety concerns including heat generation, potential phosgene generation, etc. Include appropriate engineering theory, safety, chemistry, as well as operation.
- o Training should be commensurate with education, experience, job requirements and other previous training of personnel.
- o Use lessons learned from this incident along with Savannah River Project and industry to familiarize personnel on charcoal operation and hazards.

8. General considerations:

On June 15, 1993 an internal memo was sent from Restoration & Remediation/Construction Safety to the manager of the Restoration and

Remediation division addressing the idea of the generation of phosgene during the Z9 VES off normal occurrence.

It is the opinion of the root cause analysis team that it is highly unlikely that phosgene, if it was generated, was released in the earlier phases of the event.

THIS PAGE REVISED (RLV.2)

ATTACHMENT A.2
PROCESS FLOW DIAGRAM OF THE VAPOR EXTRACTION SYSTEM

4-21-93	ARS				AS BUILT
REVISION	DATE	DWN.	CHK'D	APP'D	DESCRIPTION

SEE SHEET 2 FOR DRAWING DIRECTORY/LEGEND INFORMATION

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PLOT: 31.8,20.3 FACTOR: 1=16 ANGULAR: ± 1/2

SCALE: NONE SIZE: D DRAWING NUMBER: 24000
SHEET 5 OF 8

BARNEBEY & SUTCLIFFE CORP
PUR AIR Products Division

CUSTOMER: VES - WESTINGHOUSE HANFORD REG. NO. C0112:
TITLE: PROCESS FLOW DIAGRAM

HEPA UNIT

SCALE: NONE SIZE: D DRAWING NUMBER: 24000
SHEET 5 OF 8

A.2-3/4

REVISION	DATE	OWN.	CHK'D	APP'D	DESCRIPTION
4-22-93	ARS				AS BUILT

ATTACHMENT A.3
HANFORD FIRE DEPARTMENT REPORT OF INCIDENT

HANFORD FIRE DEPARTMENT ALARM/INVESTIGATION REPORT				Alarm/Investigation No. 286																																														
in WHC Safety D. Moak R3-54 N3-05		Contractor WHC		Operation Carbon Tetachloride Removal Area																																														
		Date 06/03/93	Time 1223	Building or Location 216Z-98		Area 200-W																																												
		Reported By POC		Payroll No.	Received By B.G. Klucas																																													
		LOSS Government None Private None		Notification POC, WHC Safety, Chief Good, DOE, AL Trego, Respiratory Protection		How Received: Fire Ph. No. _____ Alarm Box No. _____ Phone No. POC Other _____																																												
☒ ALARM ☐ INVESTIGATION																																																		
Type 1 ☐ Structure Fire 4 ☒ Flammable Liquid/Gas 7 ☐ Hazmat 10 ☐ Mutual Aid 2 ☐ Grass Fire 5 ☐ Metal Fire 8 ☐ Ambulance Assist 11 ☐ Other _____ 3 ☐ Vehicle Fire 6 ☐ Vehicle Accident 9 ☐ Rescue																																																		
Cause <table style="width:100%;"> <tr> <td style="vertical-align: top;"> FIRE RELATED 1 ☒ Process Related (i.e., burning, welding, grinding, friction, chemical reaction) 2 ☐ Smoking/Matches 3 ☐ Lightning 4 ☐ Exhaust Sparks 5 ☐ Spontaneous Ignition 6 ☐ Combustibles Near Heat or Flame </td> <td style="vertical-align: top;"> 7 ☐ Electrical 8 ☐ Other _____ MAINTENANCE RELATED 9 ☐ Broken/Frozen Sprinkler Head/Line 10 ☐ Foreign Material in Smoke Detector/Defective Detector 11 ☐ Gas Leak 12 ☐ Defective Gas Alarm </td> <td style="vertical-align: top;"> 13 ☐ Water Surge 14 ☐ FACP Defective 15 ☐ Power Failure 16 ☐ Moisture in Circuit 17 ☐ Low Water Pressure 18 ☐ Other _____ </td> <td style="vertical-align: top;"> MISCELLANEOUS 19 ☐ Air Balance 20 ☐ Malicious 21 ☐ Bomb Threat 22 ☐ Suspected Arson 23 ☐ Accidental Trip 24 ☐ Smoke 25 ☐ Other _____ </td> </tr> </table>						FIRE RELATED 1 ☒ Process Related (i.e., burning, welding, grinding, friction, chemical reaction) 2 ☐ Smoking/Matches 3 ☐ Lightning 4 ☐ Exhaust Sparks 5 ☐ Spontaneous Ignition 6 ☐ Combustibles Near Heat or Flame	7 ☐ Electrical 8 ☐ Other _____ MAINTENANCE RELATED 9 ☐ Broken/Frozen Sprinkler Head/Line 10 ☐ Foreign Material in Smoke Detector/Defective Detector 11 ☐ Gas Leak 12 ☐ Defective Gas Alarm	13 ☐ Water Surge 14 ☐ FACP Defective 15 ☐ Power Failure 16 ☐ Moisture in Circuit 17 ☐ Low Water Pressure 18 ☐ Other _____	MISCELLANEOUS 19 ☐ Air Balance 20 ☐ Malicious 21 ☐ Bomb Threat 22 ☐ Suspected Arson 23 ☐ Accidental Trip 24 ☐ Smoke 25 ☐ Other _____																																									
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Corrective Action Required (Indicate by no., order of responsibility) ☐ Fire Protection Engineer ☐ Fire System Maintenance ☐ Building Administrator ☐ Fire Department ☐ Telecommunications ☐ Other																																																		
Responding Equipment <table style="width:100%;"> <tr> <td>☐ Eng. 1</td> <td>☒ Eng. 11</td> <td>☐ Sq. 3</td> <td>☐ S-1</td> <td>☐ T-3</td> <td>☒ U-2</td> <td>☐ U-21</td> <td>☐ U-34</td> <td>☒ Other</td> </tr> <tr> <td>☒ Eng. 2</td> <td>☐ Eng. 22</td> <td>☐ Attack 1</td> <td>☒ HAZ-1</td> <td>☐ T-4</td> <td>☒ U-3</td> <td>☐ U-25</td> <td>☐ U-36</td> <td>☐ T&M</td> </tr> <tr> <td>☐ Eng. 3</td> <td>☐ Eng. 33</td> <td>☐ MX-3</td> <td>☐ HAZ-2</td> <td>☒ T-11</td> <td>☐ U-4</td> <td>☐ U-25</td> <td>☐ U-38</td> <td>☐ personnel</td> </tr> <tr> <td>☐ Eng. 4</td> <td>☐ Eng. 44</td> <td>☐ Mobile Air</td> <td>☐ T-1</td> <td>☐ T-22</td> <td>☐ U-11</td> <td>☐ U-28</td> <td>☐ U-41</td> <td></td> </tr> <tr> <td></td> <td></td> <td></td> <td>☒ T-2</td> <td>☐ U-1</td> <td>☐ U-16</td> <td>☐ U-31</td> <td></td> <td></td> </tr> </table>						☐ Eng. 1	☒ Eng. 11	☐ Sq. 3	☐ S-1	☐ T-3	☒ U-2	☐ U-21	☐ U-34	☒ Other	☒ Eng. 2	☐ Eng. 22	☐ Attack 1	☒ HAZ-1	☐ T-4	☒ U-3	☐ U-25	☐ U-36	☐ T&M	☐ Eng. 3	☐ Eng. 33	☐ MX-3	☐ HAZ-2	☒ T-11	☐ U-4	☐ U-25	☐ U-38	☐ personnel	☐ Eng. 4	☐ Eng. 44	☐ Mobile Air	☐ T-1	☐ T-22	☐ U-11	☐ U-28	☐ U-41					☒ T-2	☐ U-1	☐ U-16	☐ U-31		
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			☒ T-2	☐ U-1	☐ U-16	☐ U-31																																												
Detail of Cause Chemical reaction in container																																																		
STORY OF INCIDENT																																																		
<p>We received a call from POC reporting a barrel fire in Z-crib. Upon arrival, we found a large container with 2-3 hundred pounds of carbon tetrachloride and 2000lbs. of carbon gravel that had a black scorch mark approx. 1/3 of the way up from the bottom. Water was applied to cool down the tank, which was checked by the laser head det. and was found to be 240 deg. at scorch area. We applied water off and on for 4 hours and then after it had cooled down, it was filled with water approx. 6-7 hundred gallons. Area personnel said they would be around to check on the tank until 2100 hours. All equipment back in station and in service at 1830 hours. Note: Approx. 6500 total gallons of water used at scene.</p>																																																		
shed (How and By Whom) er from P/Ts																																																		
TOTAL MANHOURS: 144																																																		
RECOMMENDATION																																																		
None																																																		

ATTACHMENT A.4

GENERAL SPECIFICATIONS AND PROPERTIES
OF THE GRANULAR ACTIVATED CARBON

**GRANULAR ACTIVATED CARBON
VIRGIN EI-410S**

EI-410S is a 4x10 mesh virgin vapor phase carbon. This product is manufactured from selected grades of coconut shell to give the superior hardness and activity required for vapor phase applications. EI-410S is primarily used in adsorption and solvent recovery of hydrocarbons, chlorinated hydrocarbons, ketones, esters, alcohols, and aromatics.

GENERAL SPECIFICATIONS:

Iodine Number (mg/g)	minimum 1200
Activity - CCl ₄ (ASTM D 3467)	minimum 60%
Apparent density (ASTM D 2854)	typical 0.44 to 0.49 g/ml
Hardness (MIL C 17605C)	typical 97
Moisture as packed (ASTM D 2867)	maximum 5%
Ash content (ASTM D 2866)	maximum 3%

PROPERTIES:

Surface area (BET)	typical 1100 to 1250 Ms/gr
Pore volume	typical 0.50 mls/gr
pH of water extract	9.5
Specific heat at 15°C	0.65 to 0.75 Btu/lb m°F

ATTACHMENT A.5

VAPOR EXTRACTION SYSTEM OPERATIONAL DATA
RECORDED DURING INCIDENT

ALM(UA1433) ALARM (ITR-1433 HEATER OVERTEMP)

Thu Jun 10 13:34 1993

Six Minute Averages

GAC ADSORDERS SCREEN A

Trends Page 31/39

Lists

GAC IN1 FLOW

GAC IN2 FLOW

GAC IN3 FLOW

GAC OUT1 FLOW

FI1531:PV 219

FI1532:PV 0

FI1533:PV 0

FI1541:PV 0

GAC OUT2 FLOW

GAC OUT3 FLOW

GAC OUT4 FLOW

FI1542:PV 249

FI1543:PV 0

FI1544:PV 0

03/06/93

10:18:00	0	0	0	0	0	0	0
10:24:00	280	266	0	1	0	0	0
10:30:00	230	236	0	0	0	0	0
10:36:00	214	233	0	0	0	0	0
10:42:00	204	229	0	0	0	0	0
10:48:00	199	225	0	0	0	0	0
10:54:00	213	238	0	0	0	0	0
11:00:00	229	250	0	0	0	0	0
11:06:00	227	248	0	0	0	0	0
11:12:00	225	249	0	0	0	0	0
11:18:00	223	247	0	0	0	0	0
11:24:00	221	247	0	0	0	0	0
11:30:00	219	249	0	0	0	0	0

A.5-3

WHC-SD-EN-TI-203, Rev. 0

Trends

Smp Time

Previous

Next

Limits

ALH(UA1433) ALARM (UTR-1433 HEATER OVERTEMP)

Six Minute Averages

GAC ADSORDERS SCREEN A

Thu Jun 10 13:44 1993

Trends Page 31/39

List

GAC IN1 FLOW

GAC IN2 FLOW

GAC IN3 FLOW

GAC OUT1 FLOW

FI1531:PV

219

FI1532:PV

0

FI1533:PV

0

FI1541:PV

0

GAC OUT2 FLOW

GAC OUT3 FLOW

GAC OUT4 FLOW

FI1542:PV

249

FI1543:PV

0

FI1544:PV

0

03/06/93

11:30:00

219

249

0

0

0

0

0

11:36:00

216

248

0

0

0

0

0

11:42:00

215

246

0

0

0

0

0

11:48:00

213

242

0

0

0

0

0

11:54:00

211

236

0

0

0

0

0

12:00:00

212

241

0

0

0

0

0

12:06:00

209

249

0

0

0

0

0

12:12:00

206

256

0

0

0

0

0

12:18:00

207

264

0

0

0

0

0

12:24:00

38

62

0

0

0

0

0

12:30:00

0

0

0

0

0

0

0

12:36:00

-832

-832

-832

-832

-832

-832

-832

12:42:00

-999

-999

-999

-999

-999

-999

-999

Trends

Smp Time

Previous

Next

Limits

ALM(UA1433) ALARM (ITR-1433 HEATER OVERTEMP)

SIA Micro Average

BLOWER/AIR COOLR SCREEN A

THU JUN 10 13:29 1993

Trends Page 30/39

List

BLOWER 1 VACUUM		BLOWER 2 VACUUM		BLOWER 3 VACUUM		AIR COOL PRESSURE	
PTI511:PV	1	PTI512:PV	99	PTI513:PV	0	PTI520:PV	8
[AIR:COOL:TEMP]		CIRCPUMP CONTROL					
-----		-----					
TII522:PV	69	TIC1522:NV	62				
03/06/93							
10:10:00	0	73	0	59	0	0	0
10:24:00	0	75	35	64	0	9	9
10:30:00	0	65	73	61	0	7	7
10:36:00	0	65	74	60	0	7	7
10:42:00	0	65	75	60	0	7	7
10:48:00	0	66	76	60	0	7	7
10:54:00	0	66	86	61	0	7	7
11:00:00	0	68	97	62	0	8	8
11:06:00	0	68	97	62	0	8	8
11:12:00	0	68	98	62	0	8	8
11:18:00	1	69	98	62	0	8	8
11:24:00	1	69	99	62	0	8	8
11:30:00	1	69	99	62	0	8	8

Trends	Smp Time	Previous	Next	Limits
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ALH(UA1433) ALARM (HTR-1433 HEATER OVERTEMP)

Thu Jun 10 13:31 1993

Six Minute Averages

BLOWR/AIR COOLR SCREEN A

Trends Page 30/39

List

BLOWER 1 VACUUM

BLOWER 2 VACUUM

BLOWER 3 VACUUM

AIR COOL PRESSURE

PI1511:PV -999

PI1512:PV -999

PI1513:PV -999

PI1520:PV -999

~~AIR COOL TEMP~~

CIRCUMPUMP CONTROL

TIC1522:PV -999

TIC1522:PV -999

03/06/93

11:30:00	1	69	99	62	0	8
11:36:00	1	69	99	62	0	8
11:42:00	2	69	99	62	0	8
11:48:00	2	69	100	63	0	8
11:54:00	1	58	83	63	0	6
12:00:00	2	69	100	63	0	8
12:06:00	2	69	100	63	0	9
12:12:00	2	69	100	63	0	9
12:18:00	2	69	100	62	0	10
12:24:00	0	69	17	63	0	2
12:30:00	0	73	0	65	0	0
12:36:00	-832	-820	-832	-822	-832	-832
12:42:00	-999	-999	-999	-999	-999	-999

Trends

Smp Time

Previous

Next

Limits

ALM(TDAL1432) OUT OF ALARM (PRC/DEWPIT DIFFERNTL LOW LIN

Wed Jun 9 14:14 1993

Six Minute Averages

EXHAUST STACK SCREEN A

Trends Page 36/39

Lists

STACK FLOW

STACK ALPHA

STACK BETA

FI1550:PV

272

RI1552A:PV

0

RI1552B:PV

1

03/06/93

10:18:00

1

0

1

10:24:00

294

0

1

10:30:00

250

0

1

10:36:00

246

0

1

10:42:00

244

0

1

10:48:00

231

0

1

10:54:00

250

0

1

11:00:00

266

0

1

11:06:00

264

0

1

11:12:00

272

0

1

11:18:00

266

0

1

11:24:00

270

0

1

11:30:00

272

0

1

A.5-7

MHC-SD-EN-TI-203, Rev. 0

Trends	Smp Time		Previous	Next			Limits
--------	----------	--	----------	------	--	--	--------

ALH(TDAL1432) OUT OF ALARM (PRC/DEWPHI DIFFERNTL LOW LIN

Wed Jun 9 14:15 1993

Six Minute Averages

EXHAUST STACK SCREEN A

Trends Page 36/39

Lists

STACK FLOW

STACK ALPHA

STACK BETA

FI1550:PV

-999

RI1552A:PV

-999

RI1552B:PV

-999

03/06/93

11:36:00

264

0

1

11:42:00

266

0

1

11:48:00

267

0

1

11:54:00

259

0

1

12:00:00

264

0

1

12:06:00

279

0

1

12:12:00

289

0

2

12:18:00

306

0

2

12:24:00

79

0

2

12:30:00

1

0

2

12:36:00

-030

-032

-032

12:42:00

-999

-999

-999

12:48:00

-999

-999

-999

A.5-8

WMC-SD-EN-TI-203, Rev. 0

Trends

Snap Time

Previous

Next

Limits

ATTACHMENT A.6
GRANULAR ACTIVATED CARBON SERVICE CONTRACT
STATEMENT OF WORK

Attachment "A"
W-204459-LR
Rev. 1

GRANULAR ACTIVATED CARBON CANISTER SERVICE CONTRACT

STATEMENT OF WORK

Introduction

The Westinghouse Hanford Company (referred to as the "Buyer" in this document) is authorized in behalf of the US Department of Energy, Richland Field Office (DOE-RL) to provide waste management for the Hanford Site. The Buyer is currently seeking an organization (referred to as "Seller" in this document) to provide granular activated carbon (GAC) canisters to support a carbon tetrachloride (CCl_4) cleanup project. The Seller shall provide for proper transportation of the GAC canisters, regeneration and return of the GAC canisters, and disposal of the waste CCl_4 in a safe and workmanlike manner.

Background

From 1955 until 1973, three soil discharge sites received CCl_4 waste mixtures from the Plutonium Finishing Plant (PFP) treatment processes. It is estimated that between 100K to 400K liters of CCl_4 was discharged at each site. The CCl_4 is mainly in the vapor phase in the unsaturated or vadose soil zones under the discharge areas. A significant amount of CCl_4 has migrated outside the discharge boundary. The discharge sites also contain other volatile organics such as tributyl phosphate (TBP), dibutylbutylphosphonate (DBBP), and their degradation products, for example dibutyl phosphate (DBP), in much lesser amounts.

Due to the concern that the CCl_4 plume may potentially contaminate the underlying groundwater on December 20, 1990, the U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology issued a letter requiring DOE-RL and the Buyer to reduce or stabilize the CCl_4 soil contamination beneath the PFP disposal sites. It was thought that by removing the CCl_4 from the vadose zone it would mitigate the potential contamination of the groundwater in the 200 West Area of the Hanford Site.

System Description

The Buyer intends to pull soil gas from unsaturated soils using a vapor extraction system (VES) which utilizes GAC canisters to remove the CCl_4 . The VES will vent up to 1500 cubic feet per minute (scfm) of soil gas from existing wells at each of two sites. A system of HEPA filters will remove any particulate radiological contaminants prior to transferring the soil gas to GAC canisters. This is to ensure that the GAC will not contain any radionuclides when sent to the seller. The GAC must remove the CCl_4 vapors to a level of 5ppm, prior to discharging the effluent to the atmosphere.

The GAC canisters will be operated with three trains in parallel, each train consisting of two canisters in series. Each train will process a maximum of 500 scfm of soil gas. The activated carbon shall be capable of removing CCl_4

Attachment "A"
W-204459-LR
Rev. 1

at a maximum rate of 500 lbs/day from two similar waste sites. The operating parameters for each site are:

- Nominal concentration of CCl_4 in the inlet is 1000 ppm;
- Maximum total flow rate is 1500 scfm;
- Maximum inlet temperature is 100°F;
- Stream relative humidity will not exceed 50%;
- Blower discharge pressure 5 psi maximum;
- CCl_4 production goal is 500 lbs/24 hr from each of two sites;
- The highest volatile organic compound readings from 30 stream analyses was:

COMPOUND	ug/mL AIR
carbon tetrachloride	6.10
chloroform	0.05
MEX 2-Butanone	0.46

It should be noted that the VES will be pulling from a number of wells to:

- 1) Maximize the production from the wellfield by quantitatively removing the CCl_4 to mitigate the potential contamination of the groundwater; and
- 2) Optimize the removal by monitoring the inlet concentrations and moving to other wells when the concentration begins to drop off.

To ensure that radioactive contaminants do not penetrate the HEPA system and enter the GAC canisters, the system has inline monitors to measure both alpha and beta emitter concentrations. Automatic system shut down will occur when radiological operating parameters upstream of the GAC canisters are exceeded. Sampling ports in the system will allow redundant radiological analysis by the Buyer's laboratory. The VES has a similar sampling set-up to measure the chemical concentrations in the soil gas.

Service Contract Requirements

The Service Contract shall be for one (1) year with a one year renewal option. The Seller shall provide:

- Initial load of 24 GAC canisters (12 at each site) plus a 2 week supply of 12 in an inventory yard where canisters will be exchanged. This is to provide for uninterrupted operation between canister exchanges.
- Exchange canisters contaminated with waste CCl_4 for regenerated canisters on a two week schedule. Twelve unused canisters must always be available for VES use.
- An activated carbon, in canisters, capable of adsorbing approximately 1000 lbs. per day from the two sites.

Each GAC canister shall:

- The activated carbon must be capable of adsorbing a minimum of 30% CCl_4 by weight in processing the soil gas.

Attachment "A"
W-204459-LR
Rev. 1

- Contain about 1500 - 2000 pounds of activated carbon.
- Allow for movement by forklift.
- Be constructed of volatile organic compound corrosion resistant material.
- Serve as shipping containers for CCl_4 contaminated GAC compliant to DOT regulations.
- Be designed and acceptable for operation in series or parallel applications.
- Provide a readily accessible CCl_4 sampling mechanism.
- Have inlets and outlets fitted with valved 6" male Camlock^R (or instant lock) couplers with end caps.

The activated carbon shall meet the following minimum specifications for gas phase removal of carbon tetrachloride:

- Activated carbon to be coal or coconut based capable of a Hardness Number greater than 90 and shall be regenerable;
- 4 X 6, 4 X 8, 4 X 10 or 6 X 16 size (U.S. Sieve);
- Total Surface area greater than 1000 m^2/g ;
- Iodine Number greater than 1000 and carbon tetrachloride adsorption capacity of 60%;
- Apparent Density - 0.47 to 0.50 g/cc, Bulk Density - 30 lb/ft^3 ;
- Ash Content, Maximum - 10%; and
- Moisture Content - 2%, maximum.

General Requirements

The Seller shall provide the personnel, transportation, and facilities necessary for proper treatment, disposal and recycling of nonradioactive waste CCl_4 contaminated GAC canisters generated at the Hanford Site. Seller shall transport from the Hanford Site, Richland, Washington, the nonradioactive waste CCl_4 , as described on the manifests, waste profile sheets, and other supporting documentation. Seller shall manage the waste submitted under this order in accordance with Code of Federal Regulations (CFR) Title 40, Parts 260-271, Washington Administrative Code (WAC)-173-303, and all other valid and applicable local, State and Federal regulations, statutes, ordinances, orders and rules.

Attachment "A"
W-204459-LR
Rev. 1

The Seller shall accept and transport all Hanford Site generated nonradioactive CCl₄ cleanup project waste (when accompanied with the necessary documentation) on a bi-weekly schedule to be determined by the Buyer's Technical Representative. GAC canisters must be supplied in sufficient quantities to maintain uninterrupted operations between canister exchanges.

The Seller shall review and approve of the manifests and supporting documentation prepared by the Buyer in a timely manner. The Seller's review/approval phase shall be completed prior to the waste leaving the Site.

Waste shall be properly transported by the Seller to their facility where the labor, materials, and equipment will be provided for proper waste management in accordance with all valid and applicable Federal, State, and local requirements. While Seller is solely responsible for any and all manner or means used to perform under this Order, recycling or reclamation should be the primary method of disposal whenever feasible. Seller shall certify and warrant its compliance with all Federal, State and Local requirements and regulations.

The Seller shall own or operate a Treatment, Storage, and Disposal Facility (TSDF) permitted by the Environmental Protection Agency (or be operating under interim status). The Buyer will submit waste only to the Seller's one receiving facility (to be specified in the submittal).

All Facilities (other than the one designated receiving facility) used during the management of the Buyer's waste will be considered a subcontractor (even if it is a subdivision of the primary contractor). The Seller shall be responsible for ensuring that subcontractors meet all requirements and conditions of the order. The Seller shall be responsible for manifesting and dispersing the waste to the final disposal facilities (if necessary). The Seller shall sign as the generator on the new manifest.

After purchase order award, the Seller shall be expected to maintain an auditable file capable of tracking the Buyer's waste to final disposition. The tracking system may be verified during a pre-award inspection.

The Seller shall indemnify the Buyer and the Government against any and all liabilities, claims, losses, damages or expenses (including attorney's fees) which may be incurred or sustained by the Seller or the Government in connection with Seller's use, misuse or handling of waste obtained under this Order.

The Seller shall notify the buyer in writing immediately upon cancellation of transportation and/or environmental insurance policies. The Seller shall notify the buyer 30 calendar days in advance of any material changes or reduction in coverage under transportation and environmental insurance policies.

Seller shall, upon final disposition of all Hanford CCl₄ cleanup project generated waste offered for disposal, provide the Buyer with a Certificate of Treatment, Disposal or Destruction (CT/D) signed by an authorized officer of

Attachment "A"
W-204459-LR
Rev. 1

the company. The minimum of information on the certificates of destruction shall include the manifest number, container item number, date of shipment, and the date/location/method of waste disposal for each item listed on the manifest. The Seller shall be able to produce Invoices and CT/D's specifically for each manifest (item for item) prior to compensation for services.

The Seller shall have documented and implemented procedures (or an equivalent documentation system) for onsite and transportation emergencies.

Upon award of the order, the Seller shall provide the Buyer with a copy of their most current Part A and B Permit Applications. The Buyer will return the Permits at the conclusion of the Purchase Order's period of performance.

The Seller shall be familiar with the Buyer's radiation release procedures and protocols for compliance with local regulatory requirements.

The Seller shall strictly comply with the Buyer's safety requirements and Onsite Services Provisions when operating at the Buyer's facility. The Buyer and the Seller shall both have the authority to "stop work" whenever a safety concern is identified.

The Buyer will provide support (operators, Health Physics, crafts, escorts, etc.) for transferring waste onto the Seller's vehicle (if needed) at no cost to the Seller. The Seller is responsible for properly loading, securing and transporting the waste in accordance with all Local, State and Federal transportation regulations. The Seller shall obtain all applicable permits prior to taking possession of the waste.

Waste Transport

The Buyer will properly package, mark, and label all wastes covered by this Purchase Order prior to the waste pickup by the Seller. Department Of Transportation (DOT) compliance is rigidly enforced.

All waste transportation shall be performed in compliance with 49 CFR. The Seller shall transport wastes in vehicles dedicated solely to waste hauling. Seller's drivers shall be trained in proper waste handling procedures, personal protection, regulatory compliance, and spill emergency response. Seller's vehicles shall carry maintained spill kits, Spill Prevention, Control, and Countermeasure (SPCC) plans, and emergency response guidebooks. Title and risks to the waste obtained under this Order shall pass to the Seller when it is placed onto the Seller's vehicle at the direction of Seller's representatives.

Remedial actions on any spills which may occur during the transport of waste from the Hanford Site shall be the responsibility of the Seller. After receiving the waste, the Seller shall sign and return the "original" copy of the manifest within 30 calendar days of the shipment date.

Attachment "A"
W-204459-LR
Rev. 1

All shipments must be weighted upon arrival and departure from the Hanford Site. All shipments will require radiation monitoring and inspection for compliance with Department Of Transportation regulations prior to entering and leaving the Hanford site. The Buyer's Transportation Department located at 2355 Stevens Drive, Richland, Washington, will inspect and validate all waste shipments and co-sign the Uniform Hazardous Waste Manifest.

Seller's Facility Audits and Inspections

The Buyer reserves the right to inspect/audit Seller's facility for information purposes before and after award. Seller shall allow Buyer's personnel to access their facility. Buyer's inspection/audit team may include non-Westinghouse Hanford personnel. The audit report may be shared with other Westinghouse and Department of energy contractors. After contract award, the Seller shall allow the Buyer to inspect/audit their facility for compliance to applicable requirements at any time during the performance interval (normally on a quarterly basis, if deemed necessary).

Prior to contract award, the Seller shall notify the Buyer if any of the following conditions exist:

- Seller's Corporate Officers working under assumed names for other businesses.
- Seller's Company operating in other locations or areas of jurisdiction under different names.
- Outstanding violations, citations, or pending actions promulgated against the Seller's Company or Subcontractors by a regulatory agency.

During the Order's period of performance, the Seller shall immediately notify the Buyer in writing if any of the above conditions occur and including, but not limited to:

- Violations, citations, or pending actions promulgated against the Seller's Company or Subcontractors by a regulatory agency.
- Significant changes to the operations or organization of the Seller's Company.

The Seller, or it's subcontractors, shall perform corrective actions on items disclosed during the buyer's inspections/audits. If the Seller, or it's subcontractors, refuse or are unable to perform such corrective action in a timely manner, the Buyer reserves the right to terminate this Order, in whole or in part, for convenience or default pursuant to the Termination provisions in this Order.

Subcontractors

The Buyer's right of access applies to all tiers of the procurement. The Seller shall provide Buyer with a list of its subcontractors which may be utilized during the transportation and/or disposal phases of the Buyer's wastes. All subcontractors utilized by the Seller shall be fully permitted (if required) for the activities performed. The Buyer, designated

Attachment "A"
W-204459-LR
Rev. 1

representative, and/or Buyer Environmental personnel may (if deemed necessary) inspect/audit all subcontractors. This is applicable before and after award of the Order. The Seller shall notify Buyer in writing of any changes made to the subcontractors list during this Order's period of performance. The Seller is encouraged to participate in the subcontractor audits. The Buyer reserves the right to reject a proposed subcontractor.

Records

All records associated with the Buyer's wastes shall be maintained by the Seller in a method compliant with the requirements specified in WAC 173-303, 40 CFR parts 260-271, or any other applicable regulations.

Laboratory Analysis and Waste Samples

The Seller shall have documented and implemented procedures for waste sample "Chain of Custody". Test reports shall be clearly traceable back to specific wastes. Reports documenting laboratory analyses shall be signed and certified by an authorized representative of the Seller. All laboratory analysis work must be performed in compliance with the test methods defined in 40 CFR part 261 and Solid Waste (SW) 846. Waste analytical work performed by the Seller shall be adequate to properly characterize and designate the waste for acceptance/disposal at the Seller's facility.

Any laboratory utilized for waste sample analysis under this order shall have a documented and implemented Quality Program as specified under the requirements of SW 846. If the Seller utilizes a subcontractor for performance of sample analysis under this order, the subcontractor's quality program shall also be subject to review and approval.

ATTACHMENT A.7

ENVIROTROL, INC. RECOMMENDED OPERATING CONDITIONS

ENVIROCONTROL, INC.432 Green Street, P.O. Box 61 • Sewickley, Pennsylvania 15143-0061
(412) 741-2030 • FAX 412-741-2670

January 8, 1993

RECEIVED

JAN 12 1993

EBASCO - RICHLAND

Mr. Mark Dippre
Ebasco Services
1201 Jadwin Ave., #202
Richland, WA 99352

RE: Westinghouse Hanford Company - Carbon Adsorbers

Dear Mr. Dippre:

I am writing in response to your recent request for technical data on the vapor phase activated carbon adsorption equipment delivered to Westinghouse Hanford company. The recommended and design operating conditions are listed in the table below. The pressure drop vs flow data is incorporated into the graph on the attached page.

	<u>Recommended (Maximum)</u>	<u>Design (Maximum)</u>
Flow:	500 CFM	650 CFM
Temperature:	100 °F	150 °F
Pressure:	5 PSIG	30 PSIG
Humidity:	50 %	100 %

I hope this information is sufficient for your requirements. Please inform me of any recommendations made to Westinghouse which will change the operating conditions of my equipment from those which are specified in the contract document.

Please feel free to give me a call if you have any additional questions.

Sincerely,

William D. Zinsser
Sales Engineer

WDZ/lp

APPENDIX B

REFERENCES PERTINENT TO THE CANISTER OVERHEATING INCIDENT

CONTENTS

B.1.0 BACKGROUND	B-1
B.2.0 PURPOSE OF DOCUMENT	B-1
B.3.0 SUMMARY OF REFERENCES	B-2
B.3.1 Summary of Adams et al.	B-2
B.3.2 Summary of ASTM (D 5160-91)	B-2
B.3.3 Summary of ASTM (D 5228-92)	B-2
B.3.4 Summary of ASTM (D 5158-92)	B-3
B.3.5 Summary of ASTM (D 4607-86)	B-3
B.3.6 Summary of ASTM (D 3838-80)	B-3
B.3.7 Summary of Boden et al.	B-4
B.3.8 Summary of Boiston	B-4
B.3.9 Summary of Bowes and Cameron	B-4
B.3.10 Summary of Calgon (1991)	B-4
B.3.11 Summary of Calgon	B-4
B.3.12 Summary of Chi and Wasan	B-5
B.3.13 Summary of Cooney	B-5
B.3.14 Summary of Graham and Ramaratnam	B-5
B.3.15 Summary of Halstead et al.	B-6
B.3.16 Summary of Harwell et al.	B-6
B.3.17 Summary of Johnson and Woods	B-7
B.3.18 Summary of Jonas and Sansone	B-7
B.3.19 Summary of Kaguei et al. (1989)	B-7
B.3.20 Summary of Kaguei et al. (1985)	B-8
B.3.21 Summary of Kovach (1978)	B-8
B.3.22 Summary of Kovach (1968)	B-8
B.3.23 Summary of Lavanchy et al.	B-8
B.3.24 Summary of Leatherdale	B-9
B.3.25 Summary of Lee and Weber	B-9
B.3.26 Summary of MSA Research Corporation	B-9
B.3.27 Summary of Meyer and Weber	B-10
B.3.28 Summary of Milham	B-10
B.3.29 Summary of Murphy and Murty	B-10
B.3.30 Summary of Naujokas	B-10
B.3.31 Summary of Naujokas (1985)	B-11

CONTENTS (cont.)

B.3.32	Summary of Noweir et al.	B-11
B.3.33	Summary of Nwankwo and Turk	B-11
B.3.34	Summary of Ozil and Bonnetain	B-11
B.3.35	Summary of Parmele et al.	B-12
B.3.36	Summary of Ruhl	B-12
B.3.37	Summary of Ruthven et al.	B-12
B.3.38	Summary of Smithson	B-13
B.3.39	Summary of Wilde	B-13

B.1.0 BACKGROUND

Three soil vapor extraction systems (VESs) are present in the Z Grid region of 200 West Area at the U.S. Department of Energy's Hanford Site near Richland, Washington. The systems are part of an Expedited Response Action (ERA) to address the potential migration of carbon tetrachloride vapors in the subsurface. An ERA is a provision included in the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) that allows accelerated cleanup activities to be undertaken at waste sites to abate imminent hazards, or to prevent significantly increased degradation of the environment that might occur if action were delayed until completion of remedial investigation feasibility study and the record of decision. The schedules for startup and operations have been aggressive since the inception of the carbon tetrachloride ERA.

One VES has been operating at the 216-Z-1A Tile Field since February 1992. This same system has been operated at the 216-Z-1B Grid intermittently. In general, the carbon tetrachloride concentrations in the soil vapor extracted from these areas are in the range of 300 to 800 parts per million by volume (ppm). A series of three canisters of granular activated carbon (GAC) is used as a treatment train to remove the carbon tetrachloride from the extracted soil gas. No significant operational problems have been encountered with this VES.

Two VESs were set up in the spring of 1993 at the 216-Z-9 Trench to remove and treat soil vapor from the wells in the area. The initial characterization of the wells demonstrated that carbon tetrachloride concentrations were in the range of 1,000 to 30,000 ppm. Well 299-W15-02 was being characterized when a GAC-filled canister overheated. At the time, the extraction process from the well had been going on for about 2 h with carbon tetrachloride concentration of 28,500 ppm, and a flow of 240 stdft³/min. Other wells in the area had been characterized for up to 7 h of extraction with similar concentrations, although at lower flow rates.

The GAC canister overheating incident was considered an offnormal occurrence. All VES operations have been halted until a better understanding of the cause of the offnormal occurrence can be determined and engineering controls are implemented to prevent a recurrence.

B.2.0 PURPOSE OF DOCUMENT

The purpose of this document is to provide a bibliography for the subject matter discussed in the body of the report and associated appendixes.

Summaries of the references are provided to expedite understanding for those unfamiliar with the technical nature of the GAC canister overheating incident. Summaries of 39 references are included in Section B.3.

B.3.0 SUMMARY OF REFERENCES

The following summaries have been written by Ebasco Environmental personnel who are familiar with the technical details of the subject matter. The summaries are organized alphabetically by author; the reference citation for each summary is the section heading.

- B.3.1 Adams, R. E., R. D. Ackley, and R. P. Shields, 1983, "Application of Impregnated Charcoals for Removing Radioiodine from Flowing Air at High Relative Humidity," *Proceedings of the Engineering Foundation*, Schloss Elmau, Bavaria, West Germany.

Adams et al. conducted laboratory tests on the effects of different commercial types of impregnated charcoals for removing radioiodine from flowing air at high relative humidity. The purpose of the tests was to determine the effects of various iodized charcoals, at both normal and abnormal operating conditions, at various levels of humidity.

In steam-air tests, the removal efficiencies for the five tested charcoals were $\geq 90\%$, at humidity of a little more than 90%. High humidity (98%) and varied room temperature did not impact the capacity for fission-product I_2 . Yet, at 100% humidity, in addition to extensive flooding of the charcoal, a drop in the removal efficiency occurred.

- B.3.2 ASTM, 1991, "Standard Guide for Gas-Phase Adsorption Testing Activated Carbon," D 5160-91, American Society of Testing and Materials, Philadelphia, Pennsylvania.

This guide covers an analysis of gas-phase adsorption testing on activated carbon, including a procedure for determining the dynamic adsorption and critical bed depth for an activated carbon used to remove a specific adsorbate from a gas stream, with test conditions chosen by the user.

The test included an activated carbon bed containing a known amount of carbon and interaction with an adsorbate in a gas stream under conditions of flow rates. The test conditions (flow rate, adsorbate concentration, temperature, pressure, and relative humidity) were determined by the user. The time for breakthrough of a specified concentration of adsorbate was measured and plotted. The procedure was repeated with varying amounts of carbon. The plot of breakthrough time versus the amount of carbon turned out to be linear. In turn the dynamic capacity and critical bed depth could be determined.

- B.3.3 ASTM, 1992, "Standard Test Method for Determination of the Butane Working Capacity of Activated Carbon," D 5228-92, American Society of Testing and Materials, Philadelphia, Pennsylvania.

This method describes the determination of butane working capacity (BWC) of new granular activated carbon. The BWC is defined as the difference between butane adsorbed at saturation and the butane retained after purging.

The test conducted included an activated bed of known volume and mass that was saturated with butane vapor. The bed was then purged under specific conditions, as determined by the user, with dry hydrocarbon-free air. From this procedure, the mass of butane per unit volume of carbon could be obtained, which is equal to the loss of mass (BWC). This procedure is useful in two areas of interest: (1) adsorption of butane and desorption with dry air and (2) effectiveness of activated carbons on other adsorbates.

B.3.4 ASTM, 1992, "Standard Test Method for Determination of Particle Size of Powdered Activated Carbon," D 5158-92, American Society of Testing and Materials, Philadelphia, Pennsylvania.

This method describes the test method for determination of the particle size of powdered activated carbon (smaller than 80 mesh) used in an air-jet sieve device.

The test required a specified amount of powdered activated carbon to be placed in a sieve that was then inserted into an air-jet sieve assembly. When air was passed through, exiting air flow was collected in a canister. The amount of carbon left on the sieve was then weighed. The particle size of carbon can be used to evaluate filter cake filtration.

B.3.5 ASTM, 1986, "Standard Test Method for Determination of Iodine Number of Activated Carbon," D 4607-86, American Society of Testing and Materials, Philadelphia, Pennsylvania.

This method describes the test method for determination of the relative activation level of iodine by adsorbing iodine from an aqueous solution. The iodine number is defined as the amount of iodine absorbed by 1 g of carbon using certain test methods.

The significance of the iodine number is that it is a relative indicator of porosity in an activated carbon; this number can be used as an approximation of surface area for some kinds of activated carbons.

B.3.6 ASTM, 1980, "Standard Test Method for pH of Activated Carbon," D 3838-80, (Reapproved 1990), American Society of Testing and Materials, Philadelphia, Pennsylvania.

This method describes the test method for determining the pH of a water extract of activated carbon.

The pH of the fluid containing an adsorbate is significant because it can be an important characteristic in understanding any type of chemical reaction that might have occurred between the activated carbon, the adsorbate containing fluid, and any other noncarbonaceous component.

- B.3.7 Boden, N., C. F. Cullis, and A. Fish, 1962, "Spontaneous Ignition in Carbon Adsorption Beds," *J. Appl. Chem.*, Vol. 12, pp. 145-148.

Boden et al. performed an experiment to clarify the cause of spontaneous ignition in carbon adsorption beds. The results indicated the phenomenon is generally due to exothermic reaction between carbon and oxygen, which is catalyzed by metal oxide impurities that may be present. When the temperature is increased, it results in a homogeneous reaction between the oxygen and solvent, resulting in spontaneous ignition.

- B.3.8 Boiston, D. A., 1968, "Acetone Oxidation," *British Chemical Engineering*, Vol. 23, No. 1, pp. 85-88.

In this safety study, it is shown that if a solvent like acetone is exposed to high temperatures, acetone oxidation can occur resulting in a sufficient amount of heat to fire the carbon. Also discussed is the influence of acetone concentration, air availability and velocity, and moisture on the reaction.

- B.3.9 Bowes, P. C. and A. Cameron, 1971, "Self-Heating and Ignition of Chemically Activated Carbon," *J. Appl. Chem. Biotechnol.*, Vol. 21, pp. 244-250.

This study is very similar to that discussed in Section B.3.17, the difference being the focus on ignition and self-heating during transportation of carbon. This study primarily focuses on the distinction between a long-term and short-term self-heating process. The primary factor in the process is the standard "weathering" time; other factors are the dependence on moisture equilibrium, temperature of carbonization, and elevated temperatures.

- B.3.10 Calgon, 1991, *Carbon Bed Fires*, Calgon Carbon Corporation, San Mateo, California, October 1991.

Calgon Carbon Corporation discusses the various causes of carbon bed fires and points out different ways to avoid them. In summary, it is recommended that a ketone carbon absorption system should not operate in a nonregenerable mode; doing so creates an extremely unsafe atmosphere and will most probably result in a bed fire at some point.

- B.3.11 Calgon, *Estimated Heats of Adsorption of Gases and Vapors on BPL Activated Carbon*, Calgon Carbon Corporation, Pittsburgh, Pennsylvania.

Calgon Carbon Corporation presents a way to calculate an estimate of total heats of adsorption of gases and vapors on BPL activated carbon in the medium of a graph. The method is intended to give a good estimate for most organic gases and solvent vapors. An example for calculating total heat of toluene adsorption on type BPL carbon is presented in a sample calculation.

- B.3.12 Chi, C. W. and D. T. Wasan, 1970, "Fixed Bed Adsorption Drying," *AIChE Journal*, Vol. 16, No. 1, pp. 23-31.

This article reports a study of both isothermal and adiabatic adsorption/desorption in a simple water vapor and hygroscopic salt system. However, the same mechanisms apply as in a solvent vapor adsorbed by activated carbon scheme. After developing the isothermal case, the authors dismiss it as being unrealistic with respect to real work situations.

For the adiabatic case, four mass and heat transfer partial differential equations, an equilibrium relationship, and four initial/boundary equations are derived. Dimensionless time and distance variables are defined and put into the equations, which are then solved numerically by computer.

The numerical solution is shown to have good agreement with experimental data. However, a very limited range of the variables was used for this simple system. Application to the much wider range of conditions found at the Hanford Site would require additional work. As an example, the authors discuss how crucial accurate determination of mass and heat transfer coefficients is to the predictive solution and then assume that the coefficients are constant over the small range of variables studied in this work. It is unlikely that the assumption of constant coefficients would apply to the GAC overheating incident.

- B.3.13 Cooney, D. O., 1974, "Numerical Investigation of Adiabatic Fixed-Bed Adsorption," *Ind. and Eng. Chem. Process Design and Dev.*, Vol. 13, No. 4, pp. 368-373.

Cooney reports a purely mathematical parameter study; no experimental data are used for comparison. The model is based on two partial differential equations for the solid phase, two partial differential equations for the gas phase, and the Langmuir equilibrium equation. Dimensionless variables are introduced and the equations solved numerically using finite differences with time increments of 0.5 s and distance increments of 0.5 cm. The case analyzed is high pressure (500 psig). Parameters used are generally "in the ballpark" of the GAC/carbon tetrachloride system except for the convective heat transfer coefficient, which is lower.

A base case was calculated and a parameter study was done for (1) the effect of lowering the inlet gas concentration, (2) reducing the K_p and h transfer coefficients, and (3) reducing the ΔH_{Ad} . Lowering the inlet gas concentration from 10% to 2% reduced the rate of travel of the temperature and mass waves. Reducing the coefficients by a factor of four spread out the wave profiles, caused the peaks T_g and T_s to drop, and increase $(T_s - T_g)$ dramatically. Reducing the heat of adsorption caused less heat to be generated, which allowed more adsorption to occur with a slower rate of travel of the mass wave. Surprisingly, peaks T_g and T_s increased.

- B.3.14 Graham, J. R. and M. Ramaratnam, 1993, "Recover VOCs Using Activated Carbon," *Chemical Engineering*, pp. 6-12.

This article explores the uses of activated carbon in recovering volatile organic compounds (VOCs). It discusses the advantages--high surface

area per unit weight, intricate pore structure, and hydrophobic surface. It highlights important parameters to consider, including (1) carbon working capacity, (2) nature of the carbon, (3) regeneration considerations, (4) nature of the VOC, and (5) inlet VOC concentration. Favorable conditions include a situation where the following are present: only one VOC, minimal particulate matter, inlet temperatures less than 120 °F, low relative humidity, and VOC concentrations <25% of the lower exposure limit.

- B.3.15 Halstead, M. P., A. Prothero, and C. P. Quinn, 1973, "Modeling the Ignition and Cool-Flame Limits of Acetaldehyde Oxidation," *Combustion and Flame*, Vol. 20, pp. 211-221.

This paper describes an experimental ignition and cool-flame limit diagram for the oxidation of equimolar mixtures of acetaldehyde, oxygen, and argon. The primary finding was that to fit the shape of the ignition boundary, a second branching reaction was necessary: the decomposition of hydrogen peroxide. The author notes the reaction is important only at high temperatures.

- B.3.16 Harwell, J. H., A. I. Liapis, R. Litchfield, and D. T. Hanson, 1980, "A Non-Equilibrium Model for Fixed-Bed Multi-Component Adiabatic Adsorption," *Chemical Engineering Science*, Vol. 35, pp. 2287-2296.

This paper discusses binary adsorption (benzene and cyclohexane) as well as discussion and findings applicable to single adsorbate systems. It states that mass and thermal wave interactions can be very complex due to the effect of temperature changes in the system. Also, assumptions of local equilibrium are only valid for dilute (i.e., low concentration) systems; otherwise, rate limiting equations must be utilized.

Two heat and two mass transfer partial differential equations with numerous boundary conditions are presented. Dimensionless variables are then defined and a solution using the "method of characteristics" is presented. The authors state that a numerical solution requires 20 min of computer time on a high-speed, mainframe computer.

Thermal waves in both the solid and fluid move ahead of mass waves. Upstream of the mass transfer zone (MTZ) the solid temperature is greater than the gas temperature because of retained heat of adsorption. Within the MTZ the two temperatures are roughly equal. Downstream of the MTZ the solid temperature is less than the gas temperature because of no heat adsorption. The peak temperatures are always associated with the initial appearance of the mass wave.

Equilibrium is only applicable to dilute systems. Rate limiting mechanisms come into play for more concentrated gas inlet situations. There is always a dynamic interaction between the mass and thermal waves that strongly influences the system performance.

- B.3.17 Johnson, J. E. and F. T. Woods, 1971, "Flammability of Activated Charcoal Used in Air Purification," *Journal of Fire and Flammability*, Vol. 2, pp. 141-156.

This study looks into the ignition and combustion hazards of activated charcoal under certain conditions. The primary focus is the nature of the major combustion products. Also addressed are variable conditions, including ignition at atmospheric pressure (static conditions), spontaneous ignition at elevated pressures, effect of air flow rate, effect of charcoal sample size, and effect of oxygen-enriched atmospheres.

- B.3.18 Jonas, L. A. and E. B. Sansone, 1981, "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon," *American Chemical Society*, Vol. 15, No. 11, pp. 1367-1369.

This experiment's purpose was to study the desorption rate of carbon tetrachloride from activated carbon. A mathematical equation was developed, with a purpose to obtain the maximum desorption rate of the carbon under the applied conditions of the test. The results of this model allowed for calculation of the regeneration of the bed in correlation to time.

- B.3.19 Kaguei, S., L. W. Shemilt, and N. Wakao, 1989, "Models and Experiments on Adsorption Columns with Constant Wall Temperature - Radially Varying and Radially Lumped Models," *Chemical Engineering Science*, Vol. 44, No. 3, pp. 483-491.

Two theoretical models for mass and thermal wave prediction in adsorption columns were developed. The first, more general, model assumed a radial temperature profile within the column and the second assumed a uniform temperature across the column cross section. A complete slate of four mass transfer and four heat transfer equations along with boundary conditions and dimensionless variables were presented. The solution used Laplace transforms.

Some of the assumptions made in the model development were as follows: (1) linear adsorption isotherms, (2) plug flow of the gas phase, (3) no temperature or concentration gradients within the particles, and (4) temperature and concentration changes did not affect heat and mass transfer coefficients.

Model predictions were compared to experimental data collected for carbon dioxide adsorbed on carbon. A technique for estimating the heat of adsorption based on comparison of results for the two developed models was given.

A parameter sensitivity analysis was done with the following conclusions. The adsorption equilibrium constant and the heat of adsorption had the greatest impact on the model prediction of the thermal wave. The particle thermal conductivity, the wall heat transfer coefficient, and the particle micropore mass diffusivity had significant but lesser effects on thermal wave prediction.

- B.3.20 Kaguei, S., Q. Yu, and N. Wakao, 1985, "Thermal Waves in an Adsorption Column," *Chemical Engineering Science*, Vol. 40, No. 7, pp. 1069-1076.

This paper is very similar to the 1989 paper by Kaguei et al. (Section B.3.19). After developing the mass and heat transfer differential equations, the paper presents a technique for estimating the mass equilibrium coefficient, the heat of adsorption, and the wall heat transfer coefficient. These three terms have the greatest impact on the numerical solution of the adsorption model.

The estimation of the parameters is based on temperature measurements made during the advance of the thermal wave through the column. Refer to Section B.3.19 for a more thorough treatment of the ideas of this paper.

- B.3.21 Kovach, J. L., 1978, "Gas-Phase Adsorption and Air Purification," *Carbon Adsorption Handbook*, Ann Arbor Science Publishers, Inc., pp. 331-358.

In this article Kovach examines the concept of gas-phase adsorption. Properties of gas-phase adsorption addressed include adsorption equilibrium (isotherms, isobars, isosteres, and entropy) and the dynamics of adsorption (selection of adsorbent, effect of particle size, depth of the adsorbent bed, temperature effects, concentration of adsorbate, presence and concentration of other contaminants, pressure effects, removal efficiency of the system, decomposition and polymerization of the adsorbate, intermittent operation of the adsorber, and regeneration conditions). One important supposition by Kovach is the dependence of concentration on the relationship between adsorption capacity and the surface areas (in optimum pore sizes).

- B.3.22 Kovach, J. L., 1968, "The Evaluation of the Ignition Temperature of Activated Charcoals in Air, Steam, Oxygen and Oxides of Nitrogen," North American Carbon, Inc., Columbus, Ohio.

This study evaluates the role of ignition temperature on activated charcoals in air, steam, oxygen, and oxides of nitrogen. It was discovered that fire could be avoided by including an automatic water spray system in the containment filters. By doing so the charcoal filters are kept from reaching fire hazard level temperatures. The author concluded that it is important to realize that "ignition temperature" is only a characteristic of activated charcoal if additional elements are considered, such as gas flow and composition and charcoal containment. Additionally, it is important to take precautions when air flow is intermittent; if possible, intermittent air flow should be avoided.

- B.3.23 Lavanchy, A., R. Touzani, and M. Stockli, "Numerical Simulation of Dynamic Physisorption on Activated Carbon Beds," Defense Tech. and Procurement Agency, CH-3700 Speiz and Dept. of Math. Swiss Fed. Inst. of Tech., CH-1015, Lausanne.

A numerical model is developed for dynamic adsorption/desorption process on activated carbon beds. The subject being addressed in this model is the problem of long integration times with other models. The objective of this

model is to address the need of adequate prediction capabilities for successful adsorber performance.

- B.3.24** Leatherdale, J. W., 1978, "Air Pollution Control By Adsorption," Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., pp. 371-387.

In this article, Leatherdale explains the concept of air pollution control by adsorption. The components, theory, various systems, and types of adsorbents available for carbon adsorption are defined. The history of activated carbon is explained, along with its advantages. Typical specifications are listed for activated carbon used for air purification.

- B.3.25** Lee, R. G. and T. W. Weber, 1969, "Interpretation of Methane Adsorption on Activated Carbon by Nonisothermal and Isothermal Calculations," *Canadian Journal of Chemical Engineering*, Vol. 47, pp. 60-65.

Lee and Weber qualitatively describe mass and heat transfer effects. The case studied was methane (in helium) adsorbed on carbon. Independent variables used were particle radius, bed length, and time. Dependent variables were bulk stream and particle pore gas phase concentrations, interstitial gas velocity, gas temperature, particle temperature, and wall temperature.

Computer results were compared to actual experimental data in plots of temperature and concentration versus time. In the conclusions it was noted that the nonisothermal model was a much better predictor than the isothermal model. Significant radial temperature gradients were noted. The numerical solution was strongly influenced by the particle radius since this term had a strong influence on heat and mass transfer coefficients, particle surface area, particle diffusional paths, and adsorption capacity. As a result, accurate prediction of heat and mass transfer coefficients was considered a major problem in model development.

- B.3.26** MSA Research Corporation, Division of Mine Safety Appliances Company, 1973, "Package Sorption Device System Study," Evans City, Pennsylvania.

This study examines adsorption thermodynamics, with particular attention to heat of adsorption. It is concluded that in the initial stages heat of adsorption is the highest due to the ability of the vapors to locate themselves in the smallest pores where the opposite wall attractions are the strongest. The heat of adsorption is similar to that of liquification in the final stages of adsorption. Appendix E presents the sample calculations for determining heat of adsorption using the Clausius-Clapeyron equation.

- B.3.27 Meyer, O. A. and T. W. Weber, 1967, "Nonisothermal Adsorption in Fixed Beds," *AIChE Journal*, Vol. 13, No. 3, pp. 457-465.

This was one of the earliest papers in the literature survey. It presented a verbal description of some of the fundamental mechanisms occurring in the particle: between the particle and the bulk stream and between the bulk stream and the wall.

The paper follows the usual procedure of writing six fundamental equations with boundary conditions and solving by numerical methods. Two hours of computer time on a mainframe computer were required for a solution.

Experimental work was performed in conjunction with the modeling effort. There was a large discussion of the estimation of the essential heat and mass transfer coefficients needed for modeling. In conjunction, it was noted that both heat and mass transfer zones expanded steadily along the bed length.

- B.3.28 Milham, R. C., 1968, "High Temperature Properties of Activated Carbon: Part I. Desorption of Iodine, Part II. Standard Method For Ignition Temperature Measurement," Savannah River Laboratory, E.I. Du Pont de Nemours and Co., Aiken, South Carolina.

This study is presented in two separate parts (Parts I and II). Part II is pertinent to this document. In Part II, the author develops a standard method for measuring ignition temperature in order to evaluate new types of activated carbon and the effects of variables (air flow, bed properties, impregnants, plant service). The author was able to conclude that at velocities below 7 ft/min, ignition did not occur due to lacking amounts of oxygen and accumulation of oxidation products in the bed.

- B.3.29 Murphy, J. L. and H. N. Murty, 1986, "Energy Management In A Packaging Gravure Solvent Recovery Operation," Westaco Corporation.

This lecture presented at the GRI Solvent Recovery Commission Meeting (1986) focuses on the components of solvent recovery systems, particularly in a packaging gravure plant. A general discussion on the parameters (activity, strength, and size) of carbon characteristics is included, as well as factors affecting adsorption, comparison of equilibrium and working capacity, and system operating costs. The authors conclude by examining additional factors that could impinge on efficient operation (loss of adsorption capacity and physical attrition of carbon) and the effects of seasonality.

- B.3.30 Naujokas, A. A., 1979, "Preventing Carbon Bed Combustion Problems," *Loss Prevention CEP Technical Manual*, Vol. 12, American Institute of Chemical Engineers, New York, New York, pp. 128-141.

This paper examines the role of oxidation of organic materials in an activated carbon bed during spontaneous bed ignition, in hopes of hot spot detection and prevention. Type of carbon used is an important factor in carbon bed combustion. Common factors causing carbon bed combustion are discussed in the conclusion of this report. Some factors discussed include the effects of higher molecular weight compounds, oxidation of esters and

ethers in carbon beds, how initiation reactions can occur at relatively mild conditions, suggested precautions during shutdowns, and maintenance of valves.

- B.3.31 Naujokas, A. A., 1985, "Spontaneous Combustion of Carbon Beds," *Plant/Operations Progress*, Vol. 4, No. 2, pp. 120-126.

This article examines the varying environmental conditions that cause spontaneous combustion of carbon beds. Some findings include the following: (1) under appropriate conditions, spontaneous GAC ignition can occur with or without the adsorbed organic materials; (2) the presence of aldehydes, ketones, and organic acids can increase the possibilities of spontaneous combustion; (3) higher molecular weight is an important factor; (4) aging can be a factor, with fresh carbon having higher oxidative activity than aged carbon; (5) the presence of cosolvents decreases the activity of oxidizable solvents; and (6) relatively low oxygen concentration can result in hot spots.

- B.3.32 Noweir, M. H., E. A. Pfitzer, and T. F. Hatch, 1973, "Thermal Decomposition of Carbon Tetrachloride Vapors at Its Industrial Threshold Limit Concentration," *American Industrial Hygiene Association Journal*, January 1973, pp. 25-37.

This article examines the decomposition products of carbon tetrachloride (phosgene, chlorine, hydrochloric acid) and their respective threshold limit values. The objective of the investigation was to examine the conditions under which these products are produced from carbon tetrachloride vapor at the threshold limit concentrations. Several variables were examined, including temperature on glass surface, glass surface area, glass surface with air flow rate, clean iron surface with temperature, "corroded" iron surface with temperature, content of water vapor, and contact of open flame with fuel.

- B.3.33 Nwankwo, J. N. and A. Turk, 1975, "Catalytic Oxidation of Vapors Adsorbed on Activated Carbon," *Environmental Science & Technology*, Vol. 9, No. 9, pp. 846-849.

This article presents the argument for systems using catalytic oxidation of vapors adsorbed on activated carbon. The systems discussed present an approach that emphasizes conservation of energy while still having the capability of oxidizing dilute concentrations of organic contaminants. The system is suggested in an environment of conventional incineration. One advantage of this system is the capacity of the catalytic carbon medium to be effectively multiplied by the number of cycles.

- B.3.34 Ozil, P. and L. Bonnetain, 1978, "Theoretical Prediction of Temperature Profiles in an Adsorbent Fixed-Bed," *Chemical Engineering Science*, Vol. 33, pp. 1233-1237.

This paper is very sparse in terms of explanation. It presents the results of the research without much discussion. In addition some seriously limiting assumptions are made.

Two mass transfer equations (bulk phase and micropore phase) and one heat transfer equation are developed. dimensionless variables are then defined, and a solution is presented using Laplace transforms. Numerous assumptions went into the development. Some of the more pertinent assumptions include the following: (1) incompressible fluid, (2) no radial heat losses, (3) no thermal accumulation in the fluid phase, (4) equal solid temperature and gas temperature, and (5) density and concentration independent of temperature.

The authors define two bed regions. The first is an entrance zone near the gas inlet where conditions are rapidly evolving. The second is a quasi-steady-state zone downstream from the entrance.

It was noted that the thermal wave becomes more broad as it progresses down the column. Additionally, the thermal wave can either precede or follow the mass wave depending on process conditions. The inlet concentration has a dramatic influence on the shape, amplitude, and relative position of the thermal wave.

- B.3.35** Parmele, C. S., W. L. O'Connell, and H. S. Basdekis, 1979, "Vapor-Phase Adsorption Cuts Pollution, Recovers Solvents," *Chemical Engineering*, December 31, 1979, pp. 58-70.

This article discusses the role of adsorption as a method of recovering solvents from atmospheric emissions. The main subjects covered include the role of adsorption, various conventional adsorption systems, adsorption performance, choosing an adsorbent, operation of an adsorber, steam regeneration, alternative adsorber designs, safety issues (including bed fire and hot spots), cost factors, and ways of achieving high removal efficiencies.

- B.3.36** Ruhl, M. J., 1993, "Recover VOCs Via Adsorption on Activated Carbon," *Chemical Engineering Progress*, pp. 37-41.

This article explains the elements of recovering VOCs by adsorption on activated carbon. The author emphasizes many factors when considering the purchase of a solvent recovery system; the most applicable and pertinent factor is fire suppression. The author notes that a simple and reliable system senses increases in temperature and consequently sounds an alarm. The system works by alerting the operator of a problem; the operator then closes the adsorber valves, therefore suffocating the fire due to lack of oxygen. The operator then douses the adsorber with water (from the bottom). It is critical not to spray the adsorber with water, due to rapid overpressure by steam generation.

- B.3.37** Ruthven, D. M., D. R. Garg, and R. M. Crawford, 1975, "The Performance of Molecular Sieve Adsorption Columns: Non-Isothermal Systems," *Chemical Engineering Science*, Vol. 30, pp. 803-810.

The authors start with a fundamental set of equations to describe adsorption, but then make several serious, simplifying assumptions that invalidate their results if they were to be applied to the GAC overheating

incident. They state that their solution is invalid for high solute concentrations.

Constant pattern waves are assumed, i.e., the shape of the mass and temperature waves are constant as they move through the column. This assumption implies that the gas and particle temperatures are the same; this would only occur if the thermal conductivity of the adsorbent were large. This is clearly not the case for the carbon tetrachloride/activated carbon system. In fact, the only significant heat transfer mechanism in this model is the heat loss from the bed to the wall.

The work defines three dimensionless parameters that are ultimately based on mass and heat transfer coefficients. A great deal of discussion goes into the estimation of these coefficients and their importance to the model. The authors conclude that nonisothermal effects are more important in larger diameter columns and have the effect of broadening the MTZ.

B.3.38 Smithson, G. R., "Regeneration of Activated Carbon: Thermal, Chemical, Solvent, Vacuum and Miscellaneous Regeneration Techniques," *Carbon Adsorption Handbook*, Ann Arbor Science Publishers, Inc., pp. 879-903.

This article examines the different types of regeneration of activated carbon including thermal, chemical solvent, vacuum, and other miscellaneous regeneration techniques. The author evaluates the effects of temperature, gas composition, retention time, and losses of carbon during regeneration. Further explanation is provided on the design, construction, and operation of a pilot plant facility, in particular a fluidized-bed system for regenerating spent powdered activated carbon and removal of chromium from wastewaters by carbon absorption.

B.3.39 Wilde, K., 1982, "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon," Correspondence, *Environmental Science and Technology*, Vol. 16, No. 10, pp. 731-733.

This comment is addressed to *American Chemical Society* regarding an experiment by Jonas and Sansone (Section B.3.18). The three primary complaints by Wilde are the following: (1) an incorrectly derived basic equation, (2) an incorrect rate model, and (3) an inadequate sample size. The author proceeds to discuss numerous other problems found with the experiment.

APPENDIX C
GAC EXPERT FINDINGS

WHC-SD-EN-TI-203, Rev. 0

EBASCO

September 15, 1993
ERL-WHC/93-10-L-93-244

Ms. Virginia Rohay
Technical Representative
Westinghouse Hanford Company
P.O. Box 1970 MSIN H6-06
Richland, WA 99352

SUBJECT: WHC ORDER NO. MLW-SVV-037106
TASK ORDER E-93-10, REV. A
MILESTONE 6 GAC EXPERT FINDINGS REPORT

Dear Ms. Rohay:

The following is a synopsis of the findings and recommendations of GAC expert Dr. Hari Murty, retained by Westinghouse Hanford Company during the week of July 26, 1993. Dr. Murty gave a verbal presentation regarding the GAC canister overheating incident to carbon tetrachloride ERA project personnel and WHC management on July 30, 1993.

Dr. Murty's findings are listed below.

- There was no GAC bed "fire", based on overheated GAC analysis, a visual inspection of the GAC, and historical statistics.
- The overheating incident was properly handled by onsite personnel with the knowledge that existed at the time.
- Some risk is inherent in extracting soil vapor onto GAC. Adsorption on GAC is a complex and sometimes unpredictable process. These risks are acceptable if proper controls are in place.
- The soil vapor was not sufficiently characterized, especially for oxidizable compounds, prior to the incident.
- The overheating was not caused strictly by carbon tetrachloride adsorption; oxidizable compounds in the soil vapor must be suspected.

Ms. Virginia Rohay
September 15, 1993
ERL-WHC/93-10-L-93-244
Page 2

Dr. Murty's recommendations are listed below.

- Bench-scale studies are needed to properly quantify the heat of adsorption and to determine the temperature profiles within a GAC canister during adsorption. Also, the effects of methyl ethyl ketone and water vapor as they relate to heat generation or removal from the canister should be studied. These studies should be used to define how temperature and other system parameters can be controlled.
- A representative sample of the soil gas from the incident well should be obtained by operating the VES and characterized for chlorinated hydrocarbons and oxidizable compounds.
- Full chemical analyses of the compounds adsorbed on the overheated GAC should be performed.
- Full laboratory analyses should be performed to understand the conditions required for acid-generating reactions.

If you have any comments or need additional information, please contact Mr. Richard Cameron at 943-0550.

Sincerely,

Jeffrey M. Grover, P.E.
Project Manager
Ebasco Environmental, A Division of
Ebasco Services Incorporated

JMG/drw

cc: D. Wilson (w/o att.)
J. Grover (w/o att.)
R. Cameron
M. Dippre
B. Peters
File: 2.2/3.6

APPENDIX D

RESULTS OF LABORATORY ANALYSIS AND BENCH-SCALE TESTING
REGARDING THE CANISTER OVERHEATING INCIDENT

ACRONYMS AND ABBREVIATIONS

ASTM	American Society of Testing and Materials
CCl ₄	carbon tetrachloride
COCl ₂	phosgene
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act</i>
CO ₂	carbon dioxide
ERA	Expedited Response Action
GAC	granular activated carbon
GC	gas chromatograph
HCl	hydrochloric acid
MEK	methyl ethyl ketone
MS	mass spectrometry
MTZ	mass transfer zone
ppm _v	parts per million by volume
PVC	polyvinyl chloride
VES	vapor extraction system

CONTENTS

D.1.0	BACKGROUND	D-1
D.2.0	OBJECTIVES	D-2
D.2.1	ORGANIC ANALYSES OF INCIDENT WELL HEADSPACE	D-2
D.2.2	ORGANIC/INORGANIC/PHYSICAL ANALYSES OF OVERHEATED GAC	D-2
D.2.3	THERMOGRAVIMETRIC ANALYSIS OF GAC	D-2
D.2.4	FULL-SCALE THERMOCOUPLE RESPONSE TESTS	D-2
D.2.5	BENCH-SCALE PHASE I AND PHASE II ADSORBER TESTS	D-3
D.2.6	CANISTER PAINT COUPON TESTS	D-3
D.3.0	PROTOCOL OF TESTS	D-3
D.3.1	ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE	D-3
D.3.2	ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC	D-3
D.3.3	THERMOGRAVIMETRIC ANALYSIS OF GAC	D-4
D.3.4	FULL-SCALE THERMOCOUPLE RESPONSE TESTS	D-4
D.3.5	BENCH-SCALE ADSORBER TESTS	D-4
D.3.6	CANISTER PAINT COUPON TESTS	D-5
D.4.0	TEST RESULTS	D-5
D.4.1	ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE	D-5
D.4.2	ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC	D-6
D.4.3	THERMOGRAVIMETRIC ANALYSES OF GAC	D-6
D.4.4	FULL-SCALE THERMOCOUPLE RESPONSE TESTS	D-7
D.4.5	BENCH-SCALE PHASE I ADSORBER TESTS	D-7
D.4.6	BENCH-SCALE PHASE II ADSORBER TESTS	D-8
D.4.7	CANISTER PAINT COUPON TESTS	D-9
D.5.0	CONCLUSIONS	D-9
D.5.1	ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE	D-9
D.5.2	ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC	D-10
D.5.3	THERMOGRAVIMETRIC ANALYSES OF GAC	D-10
D.5.4	FULL-SCALE THERMOCOUPLE RESPONSE TEST	D-11
D.5.5	BENCH-SCALE PHASE I ADSORBER TESTS	D-11
D.5.6	BENCH-SCALE PHASE II ADSORBER TESTS	D-12
D.5.7	CANISTER PAINT COUPON TESTS	D-12
D.6.0	CORRELATION OF TEST RESULTS	D-13
D.7.0	RECOMMENDATION	D-13
D.7.1	SAFE OPERATING LIMITS	D-13
D.7.2	FUTURE TESTING	D-14

ATTACHMENTS:

D.1	Organic Analyses of Incident Well Headspace and Organic/Inorganic/Physical Analyses of Overheated GAC	D.1-1
D.2	Thermogravimetric Analysis of Granular Activated Carbon and Carbon Tetrachloride	D.2-1

CONTENTS (cont.)

D.3	Analysis of First Full-Scale Thermocouple Response Test June 28, 1993	D.3-1
D.4	Analysis of Second Full-Scale Thermocouple Response Test July 20 to July 23, 1993	D.4-1
D.5	Bench-Scale Adsorber Tests Phase I Testing, August 4 to August 18, 1993	D.5-1
D.6	Bench-Scale Adsorber Tests Phase II Testing, November 8 to November 19, 1993	D.6-1

D.1.0 BACKGROUND

Three soil vapor extraction systems (VES) are set up in the vicinity of the Z Cribs in the 200 West Area of the Hanford Site. The systems are part of an Expedited Response Action (ERA) to remove carbon tetrachloride (CCl_4) vapors in the subsurface to prevent further contamination of the groundwater. An ERA is a provision included in the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) that allows accelerated cleanup activities to be undertaken at waste sites to abate imminent hazards or to prevent significantly increased degradation of the environment that might occur if action were delayed until completion of the remedial investigation/feasibility study and the record of decision. The schedules for startup and operations have been aggressive since the inception of the Carbon Tetrachloride ERA.

One VES has been operating at the 216-Z-1A Tile Field since February 1992. This same system has operated at the 216-Z-18 Crib intermittently. In general, the carbon tetrachloride concentrations in the soil vapor extracted from these areas are in the range of 300 to 800 parts per million by volume (ppm_v). A series of three canisters filled with granular activated carbon (GAC) is used as a treatment train to remove the carbon tetrachloride from the extracted soil gas. No significant operational problems have been encountered with this VES.

Two VESs were set up in the spring of 1993 at the 216-Z-9 Trench to remove and treat soil vapor from the wells in that area. One system has a capacity of $500 \text{ stdft}^3/\text{min}$ and the other a capacity of $1,500 \text{ stdft}^3/\text{min}$. The initial characterization of the wells demonstrated that carbon tetrachloride concentrations in soil vapor ranged from 1,000 to 30,000 ppm_v . Well 299-W15-82 was being characterized by the $1,500 \text{ stdft}^3/\text{min}$ system when one of the GAC-filled canisters overheated. Overheating was determined when an operator detected an abnormal odor and discovered a narrow band of darkened paint on the exterior of the canister. At the time, the extraction process from the well had been going on for about 2 h at a carbon tetrachloride concentration of 28,500 ppm_v and a nominal flow of $240 \text{ stdft}^3/\text{min}$. Other wells in the area had been characterized for up to several hours of extraction with comparable levels of carbon tetrachloride concentrations, although at lower flow rates (approximately 20,000 ppm_v at $108 \text{ stdft}^3/\text{min}$).

The overheating incident was declared an offnormal occurrence by responsible Westinghouse Hanford Company personnel. All VES operations have been halted until a better understanding of the cause of the offnormal occurrence is determined and controls implemented to reduce the potential for recurrence of such an event.

Appendix A summarized the available background information and provided the status of activities regarding the incident analysis and other tasks necessary to realize restart of the VES operations.

The objectives of six tests performed to better understand the overheating incident are presented in Section D.2. Section D.3 describes the test protocols, Section D.4 describes the test results, Section D.5 presents the test conclusions, Section D.6 correlates the results, and Section D.7 presents recommendations based on these results.

D.2.0 OBJECTIVES

The objectives of this report are to present the results of the physical and chemical analyses and bench-scale tests, show the correlation between the results of each test, and provide recommendations for safe operating limits based on the test results. The specific objectives of each analysis and test are described in the following sections.

D.2.1 ORGANIC ANALYSES OF INCIDENT WELL HEADSPACE

Well 299-W15-82, which was being characterized at the time of the incident, has been sampled twice, with the objective of determining the identity and concentrations of constituents that may have been present in the VES flow stream.

D.2.2 ORGANIC/INORGANIC/PHYSICAL ANALYSES OF OVERHEATED GAC

The first objective of these analyses was to sample GAC from the canister near the area of discolored paint to analyze for organic and inorganic constituents that may have been adsorbed during the incident. The second objective was to determine if the physical properties of the GAC had been altered by the overheating. This knowledge may lead to an understanding of which compounds were present during the incident, which reactions occurred, and if the GAC sustained physical damage during the overheating incident.

D.2.3 THERMOGRAVIMETRIC ANALYSIS OF GAC

The objectives of this analysis were as follows:

- Determine the temperature at which GAC begins to oxidize
- Determine the temperatures at which carbon tetrachloride desorbs
- Determine if carbon tetrachloride adsorption affects the oxidation temperature of GAC
- Determine when adsorbed water is driven off the GAC
- Determine the relative heat of adsorption as a function of carbon tetrachloride loading.

A knowledge of these parameters will aid in understanding the overheating incident and in establishing safe operating limits.

D.2.4 FULL-SCALE THERMOCOUPLE RESPONSE TESTS

The objective of these tests was to evaluate the heat transfer within a GAC-filled canister, exclusive of carbon tetrachloride adsorption. The effect of water evaporation on the heat transfer was also evaluated. This test also

determined the effectiveness of using thermocouples for internal temperature monitoring.

D.2.5 BENCH-SCALE PHASE I AND PHASE II ADSORBER TESTS

The objective of these tests was to gather data on extraction conditions suitable for operation of the field VES GAC treatment train. Two series of bench-scale tests have been performed to date.

The objective of the Phase I testing was to determine the relationship between flow, concentration, and heat generation in a bench-scale column that simulated the full-size field GAC-filled canister.

The Phase II testing primarily gathered data specific to extraction conditions suitable for operation of the field VES GAC treatment train at the 216-Z-9 Trench wellfield site. This included operating with inlet concentrations of carbon tetrachloride, methyl ethyl ketone (MEK), methylene chloride (CH_2Cl_2), and chloroform (CHCl_3). These tests were also designed to determine the likelihood of CCl_4 adsorption being the sole cause of the runaway temperatures that caused the overheating of the field canister near the 216-Z-9 Trench in the 200 West Area.

D.2.6 CANISTER PAINT COUPON TESTS

The objective of these tests was to determine the temperature at which the canister exterior paint and interior epoxy visibly degrade to the extent observed during the overheating incident. The test results were used to estimate the maximum external canister temperature and to evaluate the accuracy of heat transfer models.

D.3.0 PROTOCOL OF TESTS

D.3.1 ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE

A sampling pump pulled a gas sample from the incident well, at a depth near the perforated interval and passed the gas through an adsorption tube. The tube was then thermally desorbed into a gas chromatograph (GC) and analyzed for individual compounds using mass spectrometry (MS). Specific methodology of these tests is given in Attachment D.1.

D.3.2 ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC

A validated GAC desorption procedure was used to desorb organics and inorganics from GAC particles into a Tedlar bag (Tedlar is a trademark of SKC West Corporation, Fullerton, California). The samples were then collected by passing the gas through adsorption tubes. The tubes were thermally desorbed into a GC and analyzed for individual compounds by MS. Specific methodology of these tests is given in Attachment D.1.

The physical characteristics were evaluated according to specific American Society for Testing and Materials (ASTM) procedures. These procedures are ASTM D-2854 (apparent density), ASTM D-3467 (carbon tetrachloride activity), and ASTM D-3802 (hardness).

D.3.3 THERMOGRAVIMETRIC ANALYSIS OF GAC

A small quantity of GAC was suspended on a sensitive scale located in an air atmosphere oven that captures offgases for analysis by MS. The oxidation temperature of virgin GAC and carbon tetrachloride-saturated GAC were determined by monitoring the weight loss of the GAC, the temperature, and the mass of the offgas constituents. Additionally, the desorption temperature of adsorbed water was determined in the same manner. Specific methodology of these tests is given in Attachment D.2.

D.3.4 FULL-SCALE THERMOCOUPLE RESPONSE TESTS

Internal and canister surface temperature profiles were monitored using thermocouples as externally heated air was passed through a full-size GAC-filled canister. Inlet and outlet humidity and temperature were monitored to quantify the movement of water through the canister and determine its effect on temperatures. The specific methodology of these tests is given in Attachments D.3 and D.4.

D.3.5 BENCH-SCALE ADSORBER TESTS

Using parameters that simulated the full-size field GAC-filled canister, a total of 13 bench-scale adsorber tests were performed in a manner that allowed accurate data recording. The specific methodology of these tests is given in Attachment D.5.

Phase I testing, composed of seven tests, dosed the inlet air stream with carbon tetrachloride concentrations ranging from 1,000 ppm_v to 30,000 ppm_v. MEK, one of the more easily oxidizable organics that has been found in well samples at the 216-Z-1A Tile Field extraction site, was added at 200 ppm_v to the flow stream in the 1,000 ppm_v carbon tetrachloride test and the 5,000 ppm_v carbon tetrachloride test. Internal temperatures were monitored by thermocouples. Inlet (ambient) and outlet humidities and temperatures were monitored to quantify the movement of water through the GAC-filled column.

The test setup and conditions for the Phase II tests were basically similar to the Phase I tests. Additional thermocouples were added to the test column in a horizontal array located at the 28-in. level (at the center, at the quarter-diameter point, at the eighth-diameter point, and at the exterior wall). This array provided temperature measurements radially from the center to the perimeter of the test column.

Additional solvents were also introduced into the air stream. The concentrations of carbon tetrachloride ranged from 10,000 to 55,000 ppm_v during the six tests. MEK concentrations ranged from 200 to 1,000 ppm_v.

Methylene chloride was introduced at 200 ppm_v, and chloroform was introduced at 500 ppm_v. Tests 5 and 6 used only carbon tetrachloride in the air stream.

D.3.6 CANISTER PAINT COUPON TESTS

Coupons were prepared using canister plate steel coated with exterior paint and interior epoxy. In addition, exterior painted steel was taken from canisters that had been exposed to the weather for a period of time equal to that of the overheated canister.

An air-atmosphere oven was brought up to temperatures of concern in steps. At each step, the coupons were placed in the oven for an hour, roughly equivalent to the period of time that the canister experienced overheating during the incident. The coupons were then taken out of the oven and visually compared to unheated controls. Visual observations were recorded and photographs taken for comparative purposes. The specific methodology of these tests is given in Attachment D.6.

D.4.0 TEST RESULTS

For the purpose of this report, the term "oxidizable organics" means organic compounds that may be expected to oxidize under the conditions that existed in the GAC-filled canister during the overheating incident. The general conditions that existed during the incident are given in Appendix A.

D.4.1 ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE

The first sampling of well 216-W15-82 was conducted on June 10, 1993. The sample was drawn from below the perforated interval of this well. Monitoring of gas from the well during the sampling period detected 0 to 2 ppm volatile organics. The GC-MS analysis showed, in addition to carbon tetrachloride, oxidizable organics in the part-per-billion-by-volume (ppb_v) range. These oxidizable compounds included MEK, benzene, toluene, p-xylene, and others in lesser concentrations. No methane was detected in the sample.

The second sampling of well 299-W15-82 was conducted on June 14, 1993. The sample was drawn from above the perforated interval of this well. Monitoring of gas from the well during the sampling period detected 0 to 2,000 ppm volatile organics. The GC-MS analysis was dominated by the high carbon tetrachloride concentration (approximately 30,000 ppm_v) that made identification of trace levels of other organics difficult. However, parts-per-billion-by-volume levels of oxidizable compounds were found, which included acetic acid, hexachloroethane, trichloropropane, and naphthalene. No methane was detected in the sample. The actual test result from both of the analyses is provided in Attachment D.1.

D.4.2 ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC

The thermally desorbed gas sample taken from the overheated canister was analyzed on July 1, 1993. The GC-MS analysis showed, in addition to carbon tetrachloride, parts-per-billion-by-volume levels of oxidizable organics. These oxidizable compounds included MEK, toluene, and p-xylene. These same compounds were found in the organic analyses performed on samples taken from the well headspace. Hence, trace compounds that were present in the well were found adsorbed onto the GAC. The length of time between sample collection and analysis may have affected the analysis results.

The thermally desorbed sample of GAC from the overheated area of the canister showed that carbon dioxide (CO₂) concentration was an order of magnitude higher than found in ambient air.

The physical analyses of the overheated GAC showed that the GAC characteristics of apparent density, carbon tetrachloride activity, and hardness were not significantly different than GAC that was not subjected to overheating.

D.4.3 THERMOGRAVIMETRIC ANALYSES OF GAC

The thermogravimetric analyses were conducted on July 26, 1993 (Attachment D.2).

The first objective of these tests was to determine the temperature at which virgin GAC begins to oxidize. The tests results show that the GAC begins to oxidize at 480 °F and rapidly oxidizes at about 570 °F, as evidenced by the increasing temperature difference between the GAC and the oven. The oxidation temperatures are also supported by test results, which indicate carbon dioxide evolution, a product of GAC oxidation.

The next objective of these tests was to determine the temperature at which carbon tetrachloride desorbs. The tests showed that carbon tetrachloride desorbs at a linear rate over a temperature range of 77 °F to 540 °F (0.06%/°F), as evidenced by mass loss from the GAC. Some of the mass loss is attributable to GAC, which slowly begins to oxidize at 480 °F. The tests also showed that a broad exotherm occurs between 210 °F and 540 °F.

The next objective of these tests was to determine if adsorbed carbon tetrachloride affects the oxidation temperature of the GAC. The tests indicate that GAC oxidation begins at about 630 °F, which is 150 °F higher than the temperature at which virgin GAC began to oxidize.

The next objective of these tests was to determine when adsorbed water is driven off the GAC. The tests showed that the water was driven off at a nearly constant rate over a temperature range of 77 °F to 840 °F.

The final objective of these tests was to qualitatively compare the heat of adsorption as a function of carbon tetrachloride loading. The differential temperature curve shows that the heat of adsorption of carbon tetrachloride decreased as the carbon was loaded at a constant temperature of 86 °F.

D.4.4 FULL-SCALE THERMOCOUPLE RESPONSE TESTS

The results of these tests, conducted on June 28, 1993 and July 20, 1993 (Attachment D.3) are as follows.

- Water that is adsorbed to the GAC serves as the most significant heat sink for the heated air. Based on the specific heats and masses of GAC and adsorbed water, roughly four times as much heat is expended during desorption of water than the heat that is expended in heating the GAC.
- The heat lost from the canister walls is about 5% of the total heat input given the conditions of the test.
- Significant temperature gradients exist in the GAC. One of the thermocouples was moved down a few inches and back to its original location over a period of 20 min. A temperature difference of over 30 °F existed between these two points during this time period.
- The heat of adsorption due to water adsorption from the flow stream would add about 4% to the total heat input given the conditions of the test.
- The plateau at about 95 °F at each thermocouple appears to be the result of heat gain due to adsorption of water vapor contained in the flow stream.

D.4.5 BENCH-SCALE PHASE I ADSORBER TESTS

The results of these tests, conducted from August 4 to August 18, 1993 are listed below.

- Over a range of carbon tetrachloride concentrations of 1,000 ppm_v to 30,000 ppm_v, the maximum temperature rises in the column at simulated design flows were closely proportional to concentration.
- The maximum internal temperature reached was 270 °F. This was at the design flow and nominal carbon tetrachloride concentration of 30,000 ppm_v.
- The test at a nominal concentration of 30,000 ppm_v carbon tetrachloride did not produce an acidic GAC extract.
- Peak temperatures at each thermocouple location in the column were relatively constant as the thermal wave passed through the column.
- The width of the thermal wave increased as a function of depth in the column.
- The maximum temperature reached in the nominal 30,000 ppm_v carbon tetrachloride test was insufficient to discolor the paint to the extent experienced during the overheating incident.

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3 of 6

- Significant temperature gradients can exist in the canister. During the nominal 30,000 ppm_v carbon tetrachloride test, a temperature gradient of over 108 °F existed over a depth of 3½ in.
- The presence of 200 ppm_v MEK in the flow stream at 1,000 ppm_v carbon tetrachloride had no significant effect on the temperature rise in the column. The temperatures in the column were well below the 210 °F oxidation initiation temperature for MEK.
- The presence of 200 ppm_v MEK in the flow stream at 5,000 ppm_v carbon tetrachloride increased the internal temperature rise by approximately 5 °F. The temperatures in the column were well below the 210 °F oxidation initiation temperature for MEK.
- The outlet temperature did not reflect the temperature increases within the canister, e.g., when the peak temperature within the GAC-filled column is 50 °F over ambient, the outlet temperature only increases by 10 to 20 °F.

D.4.6 BENCH-SCALE PHASE II ADSORBER TESTS

The results of these tests, conducted from November 8 to November 19, 1993 are listed below.

- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 200 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 153.4 °F (an approximately 80 °F temperature rise above the inlet temperature).
- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 500 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 153.2 °F (an approximately 80 °F temperature rise above the inlet temperature).
- The maximum internal temperature for a carbon tetrachloride concentration of 10,000 ppm_v, with 1,000 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform was 164.7 °F (an approximately 95 °F temperature rise above the inlet temperature).
- Prewetting the GAC column lowered the maximum temperature from 153.4 °F to about 143 °F, a decrease of 10 °F. The effect of prewetting on other factors, such as adsorption efficiency, are unknown.
- The maximum temperature achieved with a carbon tetrachloride concentration of 40,000 ppm_v was 473.5 °F, a rise over the inlet temperature of approximately 405 °F. (The flow of carbon tetrachloride was interrupted for approximately 7 min, which may have impacted this test.)
- The maximum temperature achieved with a carbon tetrachloride concentration of 55,000 ppm_v was 445 °F, a rise above the inlet temperature of approximately 375 °F. This is 30 °F lower than the peak temperature of the 40,000 ppm_v carbon tetrachloride test.

- An excessive temperature condition was never reached during these tests.
- The pH testing performed on the spent GAC from each of the tests resulted in pH values ranging from 9.18 to 10.13, indicating that little or no hydrolysis of carbon tetrachloride occurred.
- Heat suppression systems could not be tested because temperatures associated with oxidation could not be achieved in the test column.

D.4.7 CANISTER PAINT COUPON TESTS

The results of these tests, conducted on August 18, 1993 and September 3 through September 14, 1993, are as follows.

- The exterior paint coupon began to turn a dark color, similar to the color experienced on the canister exterior during the overheating incident, at a temperature between 550 °F and 660 °F.
- The weathered paint coupon began to turn a dark color, similar to the color experienced on the canister exterior during the overheating incident, at a temperature between 550 °F and 660 °F.
- The interior epoxy coating began to turn a dark color at 420 °F and was blistered at 550 °F.
- Continuously ramping the temperature from ambient (72 °F) to 660 °F, without periodic cooldowns, did not affect the degree of darkening on the exterior paint coupon.

D.5.0 CONCLUSIONS

D.5.1 ORGANIC ANALYSIS OF INCIDENT WELL HEADSPACE

Part-per-billion-by-volume levels of oxidizable organics, including MEK, were found by this analysis. The concentrations of oxidizable organics would not be expected to have been high enough to contribute to significant heat generation during the overheating incident.

The sampling method employed was not likely to have obtained a sample that was representative of the soil gas entering the VES at the time of the incident. Due to the magnitude of the flow and vacuum provided by the VES, a radius of influence is established in the soil horizons adjacent to the well perforations. The sampling system employed after the incident is effective only for obtaining samples from the formation in the immediate vicinity of the perforated interval of the well. Additionally, due to the dominance of carbon tetrachloride in the samples, some organics may have been undetectable during the GC-MS analysis. It is possible that oxidizable organics could be concentrated downstream of the carbon tetrachloride adsorption front due to competitive adsorption. It has been demonstrated experimentally by two

experts that concentration increases of 50% to 100% over inlet concentrations can occur ahead of the mass transfer zone (MTZ), for compounds that have been displaced due to preferential adsorption.

D.5.2 ORGANIC/INORGANIC/PHYSICAL ANALYSIS OF OVERHEATED GAC

This analysis detected parts-per-billion-by-volume levels of oxidizable organics, including MEK at 10 ppb_v. Due to the dominance of carbon tetrachloride in the samples, some organics may have been undetectable during GC-MS analysis. It is also possible that the high temperatures that were generated during the incident caused desorption of some of the compounds of concern. Concentrations of oxidizable organics found during the analysis would not be expected to contribute significantly to heat generation during the overheating incident.

The overheated GAC did not show deterioration in physical parameters, indicating either that overheating did not affect the tested parameters or that the GAC sample was not taken from an overheated location in the canister.

D.5.3 THERMOGRAVIMETRIC ANALYSES OF GAC

These analyses established the initiation of virgin GAC and carbon tetrachloride-saturated GAC oxidation temperatures at 480 °F and 630 °F, respectively. It is uncertain why the carbon tetrachloride-saturated GAC has a significantly higher oxidation temperature. The oxidation of GAC appears to have two distinct rates, with an accelerated rate beginning at about 90 °F higher than the initial oxidation temperature.

A broad exothermic reaction occurred between 210 °F and 540 °F on the carbon tetrachloride-saturated GAC. It is possible that part of this exotherm is the result of the carbon tetrachloride hydrolysis reaction. To test this hypothesis, MS analysis of the evolved products should be performed.

Adsorbed water was driven off the GAC at a constant rate over the range of 77 °F to 840 °F. This result is unexpected since most of the water would be expected to be removed before the boiling point of 212 °F. Hence, some water must be chemically bound, which requires more energy to be released from the GAC.

Finally, the heat of adsorption of carbon tetrachloride decreased as the GAC was loaded at a constant flow and concentration. This is consistent with theory, which predicts that the more active adsorption sites are taken up initially, with a correspondingly higher heat of adsorption. Subsequently, the less active adsorption sites retain the adsorbate more weakly with a correspondingly lower heat of adsorption. An implication of this result is that although higher carbon tetrachloride concentrations generate more heat during adsorption, the amount of heat generated is less than proportional to the higher concentration.

D.5.4 FULL-SCALE THERMOCOUPLE RESPONSE TEST

This test showed that adsorbed water can serve as a significant heat sink in GAC. At a typical adsorbed water content of 5% by weight, desorption of water requires about four times as much energy as heating of the same weight of GAC.

Another significant conclusion of this test is that the temperature gradients within a GAC-filled canister are significant, with a differential of 30 °F possible over a few inches. This is one reason that the high temperatures reached in the adsorption front are not seen downstream.

Other conclusions are that the heat of adsorption of water vapor makes a minor contribution to heat input, and that natural convective heat loss lost from the canister walls is on the order of 5% of total heat input.

D.5.5 BENCH-SCALE PHASE I ADSORBER TESTS

Over the range of carbon tetrachloride concentrations of 1,000 ppm_v to 30,000 ppm_v, these tests show that the maximum temperature rise in the bench-scale adsorber tests is nearly proportional to the inlet carbon tetrachloride concentration.

Another conclusion is that the peak temperatures at each thermocouple location did not appear to increase as the carbon tetrachloride adsorption front moved through the GAC column, although the width of the heat transfer zone did increase with depth.

It was also demonstrated that the presence of MEK at 200 ppm_v has a minor effect on internal temperature rise at carbon tetrachloride concentrations of 1,000 ppm_v and 5,000 ppm_v. The maximum temperature in these cases was less than 115 °F. It has been documented in the literature that MEK oxidation initiates at 210 °F in the presence of GAC, which is a higher temperature than attained in either of these tests.

The most significant conclusion of the Phase I tests is that the maximum temperatures that were developed in the bench-scale column at a nominal concentration of 30,000 ppm_v carbon tetrachloride were insufficient to discolor the exterior canister paint. This implies that the heat of carbon tetrachloride adsorption alone is insignificant to have caused the discoloring observed during the overheating incident.

As found in the full-scale thermocouple response tests, significant temperature gradients can exist in the GAC-filled canister, with differentials of over 110 °F existing over 3½ in. of depth.

Another significant observation is that the bench-scale test failed to produce an acidic GAC extract at concentrations assumed to have existed during the overheating incident. This may be consistent with the fact that the exterior paint did not discolor at the temperatures experienced in the bench-scale tests at a nominal carbon tetrachloride concentration of 30,000 ppm_v, i.e., hydrolysis of carbon tetrachloride would have produced higher internal temperatures that lead to low pH via the formation of hydrochloric acid. This reaction is discussed in detail in Appendix F.

D.5.6 BENCH-SCALE PHASE II ADSORBER TESTS

The following conclusions are drawn from the results of the bench-scale Phase II tests.

- A VES can be operated at the 10,000 ppm_v carbon tetrachloride concentration level with other solvents present at lesser levels without generating excessive temperatures in the canister. Setting appropriate thresholds for all solvents known to be in the airstream in significant quantities will ensure that temperatures do not rise out of control.
- The heat of adsorption generated by elevated inlet concentrations of carbon tetrachloride without other solvents present cannot account for the temperatures observed during the overheating incident. It is concluded that some other mechanism or combination of mechanisms, such as oxidation, hydrolysis, or flow channelling, was involved.

In the tests involving these high carbon tetrachloride concentrations, the peak temperatures rose significantly higher than the documented 210 °F at which MEK oxidation initiates. Therefore, while the runaway temperature condition was not observed in any of the tests, the presence of MEK in conjunction with these high concentrations would likely initiate the oxidation of MEK and necessitate a form of temperature suppression to prevent the runaway temperature condition from occurring.

The results of the pH testing performed on the spent GAC from each of the tests (pH values ranging from 9.18 to 10.13) indicate that significant hydrolysis did not occur during any of the tests.

D.5.7 CANISTER PAINT COUPON TESTS

These tests showed that the temperatures required to darken the exterior canister paint are considerably higher than the maximum temperatures achieved in the bench-scale adsorber tests at a nominal concentration of 30,000 ppm_v carbon tetrachloride inlet concentration. Therefore, it can be inferred that the temperatures achieved inside the GAC canister during the overheating incident were caused by factors other than simple heat of adsorption of carbon tetrachloride at a concentration of 28,500 ppm_v.

Another conclusion is that the canister interior epoxy may be expected to darken and blister under the same exposure to high temperatures as the exterior paint. Since the canister also contained highly acidic quench water, the interior steel wall could be expected to have been exposed to acidic water once the epoxy coating was damaged.

D.6.0 CORRELATION OF TEST RESULTS

As noted previously, the incident well headspace analyses may not be representative of the flow stream at the time of the incident; therefore, it would be improper to draw conclusions about chemical or physical effects that may have taken place in the canister at the time of the incident based on this analysis of the constituents. These analyses do show however, that the parts-per-billion-by-volume levels of several oxidizable organics, including MEK, were also found in the head space and the GAC sample taken from the overheated GAC canister.

The physical testing of the overheated GAC did not show any deterioration in the parameters tested, relative to GAC which had not been subjected to overheating. Since the temperature required to discolor the paint is higher than the temperature at which accelerated GAC oxidation occurs, it is possible that the GAC sample was retrieved from a location in the canister, which was not subject to high temperatures.

The thermogravimetric analyses of the GAC produced information that indicates that it is possible to adsorb carbon tetrachloride at a nominal concentration of 30,000 ppm_v in a bench-scale test without apparently hydrolyzing carbon tetrachloride to a significant extent. This was verified by the bench-scale testing, which failed to produce an acidic pH extract when adsorbing at a nominal concentration of 30,000 ppm_v carbon tetrachloride.

Both the full-scale thermocouple response tests and the bench-scale adsorber tests show that extreme temperature gradients can exist in GAC-filled canisters. These tests also indicate that adsorbed water can serve as a significant heat sink for the heat of adsorption generated during carbon tetrachloride adsorption. Both of these tests also show that the internal temperatures do not appear to increase as a function of depth, regardless of whether the heat input is from a heated flow stream or from carbon tetrachloride-generated heat of adsorption.

The maximum temperature achieved in the bench-scale test at a nominal concentration of 30,000 ppm_v carbon tetrachloride was considerably lower than the temperature required to darken the canister exterior paint. Therefore, other mechanisms of heat generation must have contributed to the incident.

D.7.0 RECOMMENDATIONS

D.7.1 SAFE OPERATING LIMITS

The definition of safe operating limits are driven by two considerations: protection of personnel and protection of equipment.

Protection of personnel involves avoiding physical injury and minimizing exposure to toxic substances. The adsorption process, when applied to carbon tetrachloride and other soil gas constituents, has the potential for production of phosgene (COCl₂) and hydrochloric acid (HCl) (see Appendix F). The reactions that may produce these toxic and acidic compounds in the full-scale

extraction operations are initiated when high temperatures exist in a GAC-filled canister due to a high concentration of carbon tetrachloride in the entering flow stream. Based on the results of the thermogravimetric tests and bench-scale tests, it appears that the currently proposed limit of 10,000 ppm_v carbon tetrachloride inlet flow stream concentration and maximum internal canister temperature of 150 °F is relatively conservative. Under these limits, the possibility of production of either phosgene or hydrochloric acid is remote. In addition, the following operational thresholds are recommended.

- Inlet concentrations should not exceed operational levels of 10,000 ppm_v carbon tetrachloride, 500 ppm_v MEK, 200 ppm_v methylene chloride, and 500 ppm_v chloroform. If other solvents are detected in the airstream above 10 ppm_v, appropriate concentration thresholds should be established. These levels are based on a maximum gas inlet temperature of 70 °F and a maximum operational flow rate of 500 ft³/min through the canister. If either the inlet gas temperature or the initial GAC temperature rises above 70 °F, it is necessary to operate at either lower volatile organic carbon concentration thresholds or lower flow rate prevent the GAC temperatures from exceeding 150 °F.
- The temperature within the canister should not exceed 100 °F at the initiation of operation. If it does, ambient air should be forced through the canister until the temperatures fall to 100 °F or lower.

For the physical protection of the canisters, high internal temperatures and acidic conditions should be avoided. At the currently proposed operational limits, both of these conditions would be avoided.

For the physical protection of the polyvinyl chloride canister outlet hoses, GAC outlet temperatures should be limited to 150 °F. At the currently proposed operational limits, this temperature will not be exceeded.

D.7.2 FUTURE TESTING

Since organic analyses of the incident well headspace were not necessarily representative of the flow stream entering the VES at the time of the overheating incident, an attempt should be made to collect a more representative sample. This effort could take place during restart of extraction operations at 216-Z-9 Trench, at the currently established operational limits. Since the VES establishes a radius of influence in the subsurface soil, the analysis would be more representative of actual soil gas that existed during the overheating incident.

Samples of GAC should be heated to the temperature at which the exterior canister paint discolored, and then tested for the same physical properties as previously tested. This will determine if the physical tests accurately reflect overheating of the GAC.

The thermogravimetric analyses should be repeated to verify the conclusions of the first test, especially the fact that the carbon tetrachloride-saturated GAC has a higher oxidation temperature than the virgin GAC. Additionally, the offgas products of carbon tetrachloride-saturated GAC should be

analyzed to determine the temperature at which significant hydrolysis of carbon tetrachloride occurs. Since this test involves the use of very small quantities of GAC, anomalies produced by variability in individual GAC samples could be demonstrated.

The results of the bench-scale tests indicate that excessive temperatures observed during the overheating incident will not occur at inlet carbon tetrachloride concentrations below 10,000 ppm_v. Operation of the VES significantly above the 10,000 ppm_v level may require additional bench-scale testing of the following:

- Higher inlet concentrations of carbon tetrachloride should be run to determine if internal temperatures continue to increase as a function of concentration
- MEK should be tested with higher carbon tetrachloride concentrations to determine when full oxidation of MEK occurs, and to quantify its effect on internal temperature rise
- Tests at elevated concentrations of carbon tetrachloride should be rerun such that the column is fully saturated with carbon tetrachloride, to determine if the internal temperature rise increases with depth in the column
- Sampling of carbon tetrachloride along the column should be arranged so that the locations of the heat front and carbon tetrachloride MTZ can be determined
- Simulate a flow blockage in the column, for the purpose of determining if significant increases in internal temperatures occur
- Determine if higher relative humidity in the inlet flow stream can be used to reduce GAC temperatures.

ATTACHMENT D.1

ORGANIC ANALYSES OF INCIDENT WELL HEADSPACE AND
ORGANIC/INORGANIC/PHYSICAL ANALYSES
OF OVERHEATED GAC

ATTACHMENT D.1

ORGANIC ANALYSES OF INCIDENT WELL HEADSPACE AND
ORGANIC/INORGANIC/PHYSICAL ANALYSES
OF OVERHEATED GAC

The results of the organic analysis of the well headspace and the overheated GAC performed by Hanford Environmental Health Foundation are presented in Attachments D.1-1 through D.1-3. The results of the inorganic analyses of the overheated GAC, performed by Pacific Northwest Laboratory, are presented in Attachment D.1-4.

August 23, 1993

TO: Brian Peters Richland
 FROM: Philip Bartley Richland
 SUBJECT: REVIEW OF HEHF LABORATORY RESULTS FOR ACTIVATED CHARCOAL
 OVERHEATING INCIDENT

As you know, the Hanford Environmental Health Foundation (HEHF) recently provided analysis results for several Thermal Desorption Unit (TDU) tubes received from Ebasco (Attachment D.1-1) as a result of the recent activated charcoal overheating incident. These results indicated: (1) several volatile organics, including some flammables, were present in well 299-W15-82 at very low concentrations during the days of testing, (2) the field monitoring capabilities currently available are adequate for determining concentrations in GAC, and (3) HEHF's available method for this determination is effective if the concentrations are maintained very low but may not be cost effective when compared to the field method and data needs.

The TDU tubes provided to HEHF represented three days of monitoring. The first day (June 10, 1993) monitoring was performed downwell in well 299-W15-82 during a period when minimal levels of carbon tetrachloride were detected at the mouth of the well. The second day (June 14, 1993) monitoring was performed downwell in the same well during a period with normal/high levels of carbon tetrachloride. The third day (July 1, 1993) monitoring was performed on the gas resulting from thermal desorption of GAC samples taken from the canister that overheated and other canisters.

The TDU tubes used for all measurements were Carbotrap 300[®] tubes, manufactured by Supelco, Inc. These tubes were chosen due to their wide band sensitivity, acknowledged use in this type of application and the existence of a standardized procedure for analysis.

First Monitoring Day - Downwell, low concentration carbon tetrachloride

During the first day, there was little to no measurable carbon tetrachloride leaving the monitored well during TDU sampling. The OVM[®] reading at the beginning and completion of the TDU sampling was 0 with a maximum reading seen of 2.2. With the limited sensitivity of the OVM[®] to carbon tetrachloride, these readings do not preclude the presence of carbon tetrachloride, only indicate low concentrations. The Odyssey[®] also read 0 ppm. Units for the OVM[®] were purposely not included to ensure that the readings are not assumed to be ppm of carbon tetrachloride. The OVM[®] read out is in ppm.

Two TDU tubes were attached in series to a sampling train drawing air from the system at 98.5 ft depth. The SEAMIST[®] system was also at this depth. Series measurements were chosen to determine the presence and effects of tube breakthrough.

The HEHF desorbed the tubes onto a concentrating tube and desorbed this concentrating tube into a single point calibrated gas chromatograph/mass spectrometer (GC/MS) using an HEHF prepared procedure. The results indicated the presence of several volatile and semivolatile organics, some flammable, in the low ppb range (Attachment D.1-2). The effects of these organics on the overheating is unknown. With the exception of carbon tetrachloride, there was little breakthrough to the back up tube. The carbon tetrachloride breakthrough was considerable and rendered the carbon tetrachloride results unusable.

Second Monitoring Day - Downwell, high concentration carbon tetrachloride

During the second day, there was a high concentration of carbon tetrachloride leaving the monitoring well during TDU sampling. The OVM® reading averaged 2,000 at the opening.

The two TDU tubes were again attached in series. The measurement depth was 65 ft; the SEAMIST® was at 58 ft.

Due to the high concentration, a low sample volume was collected. In the laboratory, the backup tube was monitored first. Even with a low volume, the carbon tetrachloride concentration saturated the GC/MS and shut down the system. This happened several times. As a result, all readings from this evaluation are questionable. Due to the high backup tube concentration, it was determined to not desorb the first tube.

The peaks that could be identified (Attachment D.1-3) were very similar to those found in the low concentration downwell sample with two major exceptions. Hydrochloric acid and acetic acid were found in the high concentration sample. It is unknown what effect the periodic GC/MS shutdown had on the identification of these peaks.

If continued acid evaluation is necessary, one of two methods will provide at least qualitative information. In the first method, hanging Ph paper in the air stream at the entrance to the well during outgasing will identify the presence or absence of an acidic atmosphere. If this is done, another piece of pH paper should be hung in a nonexposed area to serve as a control.

In the second method, a known volume of air from the well could be bubbled through pre-tested water and tested for pH. The pH testing could be done in accordance with ASTM Standard D 4890-89, *Screening of pH in Waste*.

Third Monitoring Day - GAC Samples

GAC samples were taken from the canister that overheated and other canisters in the GAC train. These samples were thermally desorbed in the Field Monitoring Lab on July 1, 1993 using a modification of the draft GAC Desorption Procedure. This draft procedure has been validated and is awaiting internal administrative completion. These procedure identifies the steps needed to desorb a known amount of GAC at a controlled temperature and gas flow rate into a Tedlar® bag. The modification was to allow sampling of the Tedlar® bag into the TDU tubes.

With the lessons learned from the first two days of monitoring, sample volumes were again reduced. The volumes chosen for this day's samples were considered the lowest practical level needed to still achieve quantitative results.

The results of the HEHF analysis of the TDU tubes were very similar to the results seen in the Field Monitoring Laboratory (i.e., large concentrations of carbon tetrachloride and significantly lower concentration of other organochlorides). The only additional organics seen were very small amounts of toluene, p-xylene and n-hexane. Although carbon tetrachloride concentrations were different in the different canisters sampled, no concentration-based conclusions could be drawn.

The TDU levels recorded for carbon tetrachloride were lower than seen in the field laboratory due to breakthrough in the TDU tubes. The other organochloride levels were same order of magnitude but typically lower.

Conclusions/Recommendations

There were several organic compounds in the well at very low concentrations. The effect that these low concentrations had on the canister overheating is unknown. The use of TDU tubes for monitoring trace quantities of organics in the presence of higher concentrations of carbon tetrachloride is effective if the initial concentration of carbon tetrachloride is relatively low and the sample volume is strictly controlled. The Field Monitoring Laboratory provides organochloride results that are at least as good as those recorded at HEHF, particularly when high concentrations are encountered.

It is recommended that the Field Monitoring Lab be used as much as practical for organochloride monitoring. If the presence of non-organochlorines is expected, and these non-organochlorines are possibly causing some negative system effects, HEHF analysis of TDU tubes should be used under very controlled conditions.

ATTACHMENT D.1-1

HEHF ANALYSIS OF TDU TUBES FOR VOLATILE ORGANICS

HANFORD ENVIRONMENTAL HEALTH FOUNDATION

August 18, 1993

CO 19438 and 19447

EBASCO
1201 Jadwin Ave
Suite 201
Richland, WA 99352

Attn: B. Peters

ANALYSIS OF TDU TUBES FOR VOLATILE ORGANICS

The thirteen Carbotrap 300 (Thermal Desorption Unit) tubes received June 10, 14 and July 13, 1993 have been analyzed as requested for GC/MS scan. The samples were analyzed according to Environmental Health Sciences draft method HAPR70-146. This method is a semi-quantitative procedure designed to identify chemical compounds trapped on thermal desorption tubes and to give estimated concentrations of target compounds based on a single point calibration curve. The results of these analyses are descriptive and based upon computer searches of mass spectral libraries and on analyst interpretation.

Per your request, we are including the analyst's worksheet for each sample. This report consists of a tabulated quantitative analysis based on single point calibration of the target list, analyst comments containing the results of computerized library searches and copies of the chromatograms obtained for each sample. Please note that the analyst's worksheets report results to a greater number of digits than allowable given the semi-quantitative nature of this method. All data should be rounded to one significant figure (i.e. 19.47 would become 20). Raw data is stored on computer tapes and can be re-evaluated at any time.

Enclosed with this report are copies of all file documents pertaining to this report. While we may retain a copy of these items for business purposes, your copy is the record copy.

The attached table cross references your sample identification numbers with those from the laboratory.

If you have any questions about this report, please contact me at (509)-376-0222.

D. B. Bonfoey
Chemist
Environmental Health Sciences

bis

cc: P. M. Hickey, WHC, R3-54
V. J. Rohay, WHC, H6-06

August 18, 1993
Page 2

CO 19438 and 19447

Sample ID number	Laboratory ID number
W1582PCB93-1 CARBOTRAP 300	E93-6-369
W1582PCB93-2 CARBOTRAP 300	E93-6-370
W1582PCB93-4 (BLK) CARBOTRAP 300	E93-6-371
W1582PCB93-5 CARBOTRAP 300	E93-6-413
W1582PCB93-6 CARBOTRAP 300	E93-6-414
BLANK	E93-6-415
28M-S	E93-7-297
28M-B/U	E93-7-298
29B-S	E93-7-299
29B-B/U	E93-7-300
25T-S	E93-7-301
25T-B/U	E93-7-302
BLANK	E93-7-303

TDU-ANALYTICAL RESULTS

CC# 19438
SAMPLE # E93-6-370
ANALYST DBB
SUPERVISOR DWS
ANALYSIS DATE 6/14/93
DATA FILE 06147D4.D
INSTRUMENT HP5890/MSD

AIR VOLUME 5.28 L

- 1 ENTER SAMPLE INFO, AIR VOLUME,
AND ng OBSERVED
- 2 ENTER TRUE VALUES OF IS & SS
- 3 PRINT WORKSHEET BY RUNNING
MACRO: P
- 4 CLEAR WORKSHEET BY RUNNING
MACRO: C

COMPCONO	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE			NA	0.00
METHYL ETHYL KETONE	8.1		NA	0.52
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	630		NA	18.97
BENZENE	9.1		NA	0.54
n-HEPTANE			NA	0.00
FLUOROBENZENE	41.6	50	83	NA
CHLOROETHYLENE			NA	0.00
CYCLOHEXANE			NA	0.00
TRIFLUOROTOLUENE	24.7	50	49	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE	4.1		NA	0.21
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE	2.8		NA	0.08
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE	1		NA	0.04
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	11.2	25.4	44	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, hexanal, octanal and nonanal which are commonly observed in sample blanks. A significant response for Freon 113 was observed in this sample and in the blank for this sample set.

The major peak was identified as carbon tetrachloride. The high concentration of carbon tetrachloride in the sample caused a temporary detector shut-down resulting in a low estimate for the concentration of carbon tetrachloride in the sample.

The chromatogram contained several peaks at low ppb levels. The following is a list of peaks that could be identified with a good computer generated match: 2-methyl-1-propene (or 2-butene), pentadiene, 2-methyl-2-propanol, 2-methyl-2-propenal, methyl ethyl ketone, chloroform, benzene, toluene, 4-hydroxy-4-methyl-2-pentanone, a-pinene, cyclohexanone, D-Limonene and phenol. The chromatogram also contained a group of unresolved peaks at the higher boiling point end of the chromatogram. Mass spectra of individual components could not be obtained because the peaks were not resolved. In general, the group appears to be a hydrocarbon mixture. Two components of the group were identified as alkyl benzenes (trimethyl or methyl ethyl).

File: C:\CHEMPC\DATA\0614TD4.D
 Operator: DBB
 Date Acquired: 14 Jun 93 11:36 am
 Method File: TDU2.M
 Sample Name: E93-6-370
 Misc Info:
 ALS vial: 1

File: C:\CHEMPC\DATA\0614TD4.D
 Operator: DBB
 Date Acquired: 14 Jun 93 11:36 am
 Method File: TDU2.M
 Sample Name: E93-6-370
 Misc Info:
 ALS vial: 1

TDU-ANALYTICAL RESULTS

CO# 19438
SAMPLE # E93-6-371
ANALYST DBB
SUPERVISOR DWS
ANALYSIS DATE 6/14/93
DATA FILE 06147D3.D
INSTRUMENT HP5890/MSD

AIR VOLUME BLANK L

- 1 ENTER SAMPLE INFO, AIR VOLUME,
AND ng OBSERVED
- 2 ENTER TRUE VALUES OF IS & SS
- 3 PRINT WORKSHEET BY RUNNING
MACRO: P
- 4 CLEAR WORKSHEET BY RUNNING
MACRO: C

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	#VALUE!
ACETONITRILE			NA	#VALUE!
n-HEXANE			NA	#VALUE!
METHYL ETHYL KETONE			NA	#VALUE!
2-METHYL HEXANE			NA	#VALUE!
1,1,1-TRICHLOROETHANE			NA	#VALUE!
3-METHYL HEXANE			NA	#VALUE!
CARBON TETRACHLORIDE	7.1		NA	#VALUE!
BENZENE			NA	#VALUE!
n-HEPTANE			NA	#VALUE!
FLUOROBENZENE	49.3	50	99	NA
TRICHLOROETHYLENE			NA	#VALUE!
METHYLCYCLOHEXANE			NA	#VALUE!
a,a,a-TRIFLUOROTOLUENE	40.7	50	81	NA
METHYL ISOBUTYL KETONE			NA	#VALUE!
TOLUENE			NA	#VALUE!
1,1,2-TRICHLOROETHANE			NA	#VALUE!
TETRACHLOROETHYLENE			NA	#VALUE!
2-HEXANONE			NA	#VALUE!
CHLOROBENZENE			NA	#VALUE!
ETHYL BENZENE			NA	#VALUE!
p-XYLENE			NA	#VALUE!
o-XYLENE			NA	#VALUE!
p-BROMOFLUOROBENZENE	16.1	25.4	63	NA
1,1,2,2-TETRACHLOROETHANE			NA	#VALUE!

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, hexanal, octanal, and nonanal which are commonly observed in sample blanks.

A significant chromatographic peak identified as Freon 113 was observed. Freon 113 is sometimes observed in blanks but not at the high concentration observed in this blank. A minor peak identified as carbon tetrachloride at 7.1 nanograms was also observed.

File: C:\CHEMPC\DATA\0614TD3.D
 Operator: DBB
 Date Acquired: 14 Jun 93 10:42 am
 Method File: TDU2.M
 Sample Name: E93-6-371
 Misc Info:
 ALS vial: 1

TDO-ANALYTICAL RESULTS

CC# 19447
 SAMPLE # E93-7-297
 ANALYST DBB
 SUPERVISOR DWS

ANALYSIS DATE 8/4/93
 DATA FILE 0804TD7.D
 INSTRUMENT HP5890/MSD

AIR VOLUME 0.0416 L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE	1.3		NA	12.28
METHYL ETHYL KETONE	1.3		NA	10.60
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	453		NA	1731.12
BENZENE			NA	0.00
n-HEPTANE			NA	0.00
FLUOROBENZENE	44.1	50	88	NA
TRICHLOROETHYLENE			NA	0.00
METHYLCYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	40.6	50	81	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE			NA	0.00
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE			NA	0.00
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE			NA	0.00
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	16.3	25.4	64	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

Carbon tetrachloride is the major component in this sample. The high concentration of carbon tetrachloride caused the detector to temporarily shut down so that the estimated concentration of carbon tetrachloride in the sample is low. A minor peak identified as chloroform was also observed.

This sample contains peaks identified as ethanol, acetone, carbon disulfide and toluene which were also observed in the blank associated with this sample set.

File: C:\CHEMPC\DATA\0804TD7.D
 Operator: BW
 Date Acquired: 4 Aug 93 12:31 pm
 Method File: TDU2.M
 Sample Name: E93-7-297
 Misc Info: POSSIBLE SWITCH WITH E93-7-302
 ALS vial: 1

TDO-ANALYTICAL RESULTS

COW 19447
 SAMPLE # E93-7-298
 ANALYST DBB
 SUPERVISOR DWS
 ANALYSIS DATE 8/4/93
 DATA FILE C804TDB.D
 INSTRUMENT HP5890/MSD
 AIR VOLUME 0.0416 L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE			NA	0.00
METHYL ETHYL KETONE			NA	0.00
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	5.9		NA	22.55
BENZENE			NA	0.00
n-HEPTANE			NA	0.00
FLUOROBENZENE	44.4	50	89	NA
TRICHLOROETHYLENE			NA	0.00
METHYLCYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	46.2	50	92	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE			NA	0.00
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE			NA	0.00
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE			NA	0.00
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	17.6	25.4	69	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

This sample contains peaks identified as ethanol, acetone, carbon disulfide and toluene which were also observed in the blank associated with this sample set.

File: C:\CHEMPC\DATA\0804TD8.D
 Operator: BW
 Date Acquired: 4 Aug 93 1:28 pm
 Method File: TDU2.M
 Sample Name: E93-7-298
 Misc Info: POSSIBLE SWITCH WITH E93-7-302
 ALS vial: 1

File: C:\CHEMPC\DATA\0604TD8.D
Operator: BW
Date Acquired: 4 Aug 93 1:28 pm
Method File: TD02.M
Sample Name: E93-7-298
Misc Info: POSSIBLE SWITCH WITH E93-7-302
ALS Vial: 1

Sample Numbers E93-6-413 & 414
Analysis Date 6/18/93
CO# 19447 *WJS 8/17/93*

A high concentration of volatile compounds in sample number E93-6-414 caused a loss of detector vacuum and resulted in an automatic shut-down during the sample run. The GC/MS was restarted twice, but due to the time required to restart the instrument, sample data was lost.

An unidentified early eluting component with m/z values of 38, 36 and 37 eluted from 7.6 to 8 minutes then apparently caused the detector to shut down. (Data file 0618TD6.D)

The GC/MS was restarted and a high background (baseline) was noted. The mass spectra of this background is similar to the spectra of hydrochloric acid. Chromatographic peaks identified as chloroform and carbon tetrachloride eluted. The carbon tetrachloride then caused another detector shut-down. (Data file 0618TD7.D)

On restart several chromatographic peaks were observed and tentatively identified. Good computer match quality was obtained for acetic acid, 1,1,1-trichloropropane, tetrachloroethylene and hexachloroethane. There are other identification possibilities for the phenol peak. The other possibilities usually have a phenol ion in the fragmentation pattern. High background makes the positive identification of 2-ethyl-2-hexenal difficult. The mass spectra of naphthalene and azulene are similar so the peak labeled naphthalene could not be positively identified. The high background in this sample has a mass spectra similar to hydrochloric acid. (Data file 0618TD8.D)

E93-6-414 was the backup tube (second in series from the source). Due to the problems encountered in analyzing the backup tube, the source side tube (E93-6-413) was not analyzed.

File: C:\CHEMPC\DATA\0618TD6.D WHC-SD-EN-TI-203, Rev. 0
Operator: DEB
Date Acquired: 18 Jun 93 12:57 PM
Method File: TDU2.M
Sample Name: E93-6-414
Misc Info:
ALS vial: 1

File: C:\CHEMPC\DATA\0618TD7.D WHC-SD-EN-TI-203, Rev. 0
Operator: DBB
Date Acquired: 18 Jun 93 1:10 pm
Method File: TDU2.M
Sample Name: E93-6-414
Sample Info:
ALS vial: 1

File: C:\CHEMPC\DATA\0618TD8.D
 erator: DBB
 Date Acquired: 18 Jun 93 1:32 pm
 Method File: TDU2.M
 Sample Name: E93-6-414
 Misc Info:
 ALS vial: 1

TDU-ANALYTICAL RESULTS

19433
 SAMPLE # E93-6-415
 ANALYST DEB
 SUPERVISOR DWS
 ANALYSIS DATE 6/18/93
 DATA FILE 0618TD5.0
 INSTRUMENT HP5890/MSD

AIR VOLUME BLANK

L

POUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
ENTANE			NA	#VALUE!
TCNITRILE			NA	#VALUE!
HEXANE			NA	#VALUE!
THYL ETHYL KETONE			NA	#VALUE!
METHYL HEXANE			NA	#VALUE!
1,1-TRICHLOROETHANE			NA	#VALUE!
METHYL HEXANE			NA	#VALUE!
REON TETRACHLORIDE			NA	#VALUE!
HEPTANE			NA	#VALUE!
HEPTANE	48	50	96	NA
UCROBENZENE			NA	#VALUE!
ICHLOROETHYLENE			NA	#VALUE!
THYLCYCLOHEXANE			NA	#VALUE!
a,a-TRIFLUOROTOLUENE	48.6	50	97	NA
THYL ISOBUTYL KETONE			NA	#VALUE!
LUENE			NA	#VALUE!
1,2-TRICHLOROETHANE			NA	#VALUE!
ETRACHLOROETHYLENE			NA	#VALUE!
-HEXANONE			NA	#VALUE!
HLOROBENZENE			NA	#VALUE!
THYL BENZENE			NA	#VALUE!
-XYLENE			NA	#VALUE!
-XYLENE			NA	#VALUE!
-BROMOFLUOROBENZENE	29.1	25.4	115	NA
1,2,2-TETRACHLOROETHANE			NA	#VALUE!

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

File: C:\CHEMPC\DATA\0618TD5.D
 Operator: DBB
 Date Acquired: 18 Jun 93 12:01 pm
 Method File: TDU2.M
 Sample Name: E93-6-415
 Misc Info:
 ALS vial: 1

Sample E93-7-299
Data File 0804TD9.D
Analysis Date 8/4/93
DWS 8/17/93

The high concentration of carbon tetrachloride in this sample caused the detector to shut-down during the analysis run. Several peaks including chloroethane, Freon 11, ethanol, acetone, carbon disulfide methylene chloride and chloroform were observed before the detector shut-down. Freon 11 is commonly observed in sample blanks. Ethanol, acetone and carbon disulfide were observed in the sample blank associated with this sample set.

File: C:\CHEMPC\DATA\0804TD9.D
 Operator: BW
 Date Acquired: 4 Aug 93 2:22 pm
 Method File: TDU2.M
 Sample Name: E93-7-299
 Misc Info:
 ALS vial: 1

TDU-ANALYTICAL RESULTS

CC# 19447
 SAMPLE # E93-7-300
 ANALYST DBS
 SUPERVISOR DWS
 ANALYSIS DATE 8/5/93
 DATA FILE 0805TD3.D
 INSTRUMENT HP5890/MSD

AIR VOLUME 0.0312 L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE			NA	0.00
METHYL ETHYL KETONE			NA	0.00
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	546		NA	2782.02
BENZENE			NA	0.00
n-HEPTANE			NA	0.00
FLUOROBENZENE	48	50	96	NA
TRICHLOROETHYLENE			NA	0.00
METHYLCYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	45.7	50	91	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE	1.8		NA	15.32
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE			NA	0.00
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE			NA	0.00
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	26.7	25.4	105	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

This sample contains peaks identified as ethanol, carbon disulfide and toluene which were also observed in the blank associated with this sample set.

File: C:\CHEMPC\DATA\0805TD3.D
 Operator: BW
 Date Acquired: 5 Aug 93 10:12 am
 Method File: TDU2.M
 Sample Name: E93-7-300
 Misc Info:
 ALS vial: 1

File: C:\CHEMPC\DATA\0805TD3.D
Operator: BW
Date Acquired: 5 Aug 93 10:12 am
Method File: TDU2.M
Sample Name: E93-7-300
Misc Info:
ALS vial: 1

TDU-ANALYTICAL RESULTS

COW 19447
 SAMPLE # E93-7-301
 ANALYST DBB
 SUPERVISOR DWS
 ANALYSIS DATE 8/5/93
 DATA FILE 08C5TD4.D
 INSTRUMENT HP5890/MSD

AIR VOLUME 0.0312 L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE	3.9		NA	35.47
METHYL ETHYL KETONE			NA	0.00
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	359.7		NA	1832.77
BENZENE			NA	0.00
n-HEPTANE			NA	0.00
FLUOROBENZENE	42.4	50	85	NA
CHLOROETHYLENE			NA	0.00
CYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	47.2	50	94	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE	2.6		NA	22.12
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE			NA	0.00
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE	0.6		NA	4.43
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	21.4	25.4	84	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

This sample contains peaks identified as ethanol, acetone, carbon disulfide and toluene which were also observed in the blank associated with this sample set.

File: C:\CHEMPC\DATA\0805TD4.D
 Operator: EW
 Date Acquired: 5 Aug 93 11:06 am
 Method File: TDU2.M
 Sample Name: E93-7-301
 Misc Info:
 ALS vial: 1

TDU-ANALYTICAL RESULTS

COW# 19447
 SAMPLE # E93-7-302
 ANALYST DBB
 SUPERVISOR DWS
 ANALYSIS DATE 8/5/93
 DATA FILE 0805T05.D
 INSTRUMENT HP5890/MSD

AIR VOLUME 0.0312 L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE			NA	0.00
n-HEXANE	2.4		NA	21.83
METHYL ETHYL KETONE			NA	0.00
2-METHYL HEXANE			NA	0.00
1,1,1-TRICHLOROETHANE			NA	0.00
3-METHYL HEXANE			NA	0.00
CARBON TETRACHLORIDE	607.7		NA	3096.40
BENZENE			NA	0.00
n-HEPTANE			NA	0.00
FLUOROBENZENE	24.5	50	49	NA
1,2-DICETHYLENE	14		NA	83.49
METHYLCYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	23.8	50	48	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE			NA	0.00
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE	40.2		NA	189.89
2-HEXANONE			NA	0.00
CHLOROBENZENE			NA	0.00
ETHYL BENZENE			NA	0.00
p-XYLENE			NA	0.00
o-XYLENE			NA	0.00
p-BROMOFLUOROBENZENE	15.6	25.4	61	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

This sample contains peaks identified as ethanol, acetone, carbon disulfide and toluene which were also observed in the blank associated with this sample set.

A minor peak identified as chloroethane was observed and a baseline distortion with a mass spectra similar to the mass spectra of hydrochloric acid was noted.

File: C:\CHEMPC\DATA\0805TD5.D
 Operator: BW
 Date Acquired: 5 Aug 93 12:03 PM
 Method File: TDU2.M
 Sample Name: E93-7-302
 Misc Info: POSSIBLE SWITCH WITH E93-7-297
 ALS vial: 1

File: C:\CHEMPC\DATA\0805TD5.D
 Operator: BW
 Date Acquired: 5 Aug 93 12:03 pm
 Method File: TDU2.M
 Sample Name: E93-7-302
 Misc Info: POSSIBLE SWITCH WITH E93-7-297
 ALS vial: 1

TDU-ANALYTICAL RESULTS

CCM# 19447
 SAMPLE # E93-7-303
 ANALYST DBB
 SUPERVISOR DWS
 ANALYSIS DATE 8/5/93
 DATA FILE C805TD6.D
 INSTRUMENT HP5890/MCD

AIR VOLUME BLANK L

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	#VALUE!
ACETONITRILE			NA	#VALUE!
n-HEXANE			NA	#VALUE!
METHYL ETHYL KETONE			NA	#VALUE!
2-METHYL HEXANE			NA	#VALUE!
1,1,1-TRICHLOROETHANE			NA	#VALUE!
3-METHYL HEXANE			NA	#VALUE!
CARBON TETRACHLORIDE	14.7		NA	#VALUE!
BENZENE	1.8		NA	#VALUE!
n-HEPTANE			NA	#VALUE!
FLUOROBENZENE	42.3	50	85	NA
TRICHLOROETHYLENE			NA	#VALUE!
METHYLCYCLO-HEXANE			NA	#VALUE!
a,a,a-TRIFLUOROTOLUENE	32.7	50	65	NA
METHYL ISOBUTYL KETONE			NA	#VALUE!
TOLUENE	0.7		NA	#VALUE!
1,1,2-TRICHLOROETHANE			NA	#VALUE!
TETRACHLOROETHYLENE			NA	#VALUE!
2-HEXANONE			NA	#VALUE!
CHLOROBENZENE			NA	#VALUE!
ETHYL BENZENE			NA	#VALUE!
p-XYLENE			NA	#VALUE!
o-XYLENE			NA	#VALUE!
p-BROMOFLUOROBENZENE	22.4	25.4	88	NA
1,1,2,2-TETRACHLOROETHANE			NA	#VALUE!

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, Freon 113, hexanal, octanal, 6-methyl-5-hepten-2-one and nonanal which are commonly observed in sample blanks.

This blank contains peaks identified as ethanol, acetone, carbon disulfide, carbon tetrachloride, benzene and toluene. These compounds are not normally observed in TDU blanks but they were observed in samples in this sample set (E93-7-279 thru 303).

File: C:\CHEMPC\DATA\0805TD6.D
Operator: BW
Date Acquired: 5 Aug 93 1:03 pm
Method File: TDU2.M
Sample Name: E93-7-303
Misc Info: BLANK
ALS vial: 1

TDU-ANALYTICAL RESULTS

CC# 19438
SAMPLE # E93-6-369
ANALYST DBB
SUPERVISOR DWS 6/17/93
ANALYSIS DATE 6/14/93
DATA FILE C614TD5.D
INSTRUMENT HP5890/MSD

AIR VOLUME 5.28 L

- 1 ENTER SAMPLE INFO, AIR VOLUME,
AND ng OBSERVED
- 2 ENTER TRUE VALUES OF IS & SS
- 3 PRINT WORKSHEET BY RUNNING
MACRO: P
- 4 CLEAR WORKSHEET BY RUNNING
MACRO: C

COMPOUND	ng OBSERVED	TRUE VALUE	% RECOV.	AIR CONC. PPB
n-PENTANE			NA	0.00
ACETONITRILE	19.4		NA	2.19
n-HEXANE	232.7		NA	12.51
METHYL ETHYL KETONE	30.3		NA	1.95
1,1,1-TRICHLOROETHANE			NA	0.00
CARBON TETRACHLORIDE	549		NA	16.53
BENZENE	4.9		NA	0.29
n-HEPTANE			NA	0.00
FLUOROBENZENE	50.8	50	102	NA
TRICHLOROETHYLENE	66		NA	2.33
METHYLCYCLOHEXANE			NA	0.00
a,a,a-TRIFLUOROTOLUENE	42.7	50	85	NA
METHYL ISOBUTYL KETONE			NA	0.00
TOLUENE	88		NA	4.42
1,1,2-TRICHLOROETHANE			NA	0.00
TETRACHLOROETHYLENE	583		NA	16.27
2-HEXANONE	5.8		NA	0.27
CHLOROBENZENE			NA	0.00
ETHYL BENZENE	2.3		NA	0.10
p-XYLENE	7.6		NA	0.33
o-XYLENE	2.6		NA	0.11
p-BROMOFLUOROBENZENE	30	25.4	118	NA
1,1,2,2-TETRACHLOROETHANE			NA	0.00

COMMENTS

The air concentrations listed in the chart are estimates based on a single point calibration. The reporting detection limit is 20 nanograms for each compound on the target list. Air concentrations were calculated for responses below 10 nanograms only if the compound could be positively identified by the mass spectra.

Minor chromatographic peaks were observed for Freon 11, hexanal, octanal and nonanal which are commonly observed in sample blanks. A significant response for Freon 113 was observed in this sample and in the blank for this sample set.

The major peak was identified as carbon tetrachloride. The high concentration of carbon tetrachloride in the sample caused a temporary detector shut-down resulting in a low estimate for the concentration of carbon tetrachloride in the sample.

High detector responses were observed for chloroform, octane, tetrachloroethylene, decane, hexachloroethane and two unidentified C-10 hydrocarbons.

Detector responses were also observed for 3-methyl pentane, methylene chloride, methylcyclopentane, methyl ethyl ketone, benzene, toluene, 2-hexanone, trichloroethylene, 3-methyl heptane, ortho and para xylenes and ethyl benzene. Responses for acetone and acetonitrile were observed but they could not be positively identified.

The chromatogram also contained a group of unresolved peaks at the higher boiling point end of the chromatogram. Mass spectra of individual components could not be identified because the peaks were not resolved. The group appears to be a mixture of hydrocarbons.

File: C:\CHEMPC\DATA\0614TD5.D
 Operator: DBB
 Date Acquired: 14 Jun 93 12:31 pm
 Method File: TDU2.M
 Sample Name: E93-6-369
 Misc Info:
 ALS vial: 1

File: C:\CHEMPC\DATA\0614TD5.D
 Operator: DEB
 Date Acquired: 14 Jun 93 12:31 pm
 Method File: TDU2.M
 Sample Name: E93-6-369
 Misc Info:
 ALS vial: 1

EHF SAMPLING FORM: TFIH Organic/Inorganic

Page ____ of ____

ad 7:ne: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: Bentley / 053-46
 1. Employer: WHC 2. Sample Requestor: Fudalat 10. HIH Record #: _____
 3. 189233 / 19435 4. Case#: 22-0229 11. Exposure Group: (circle one)
 Farm: 2412 Area: E(W) 6. Location/Tank: 0 Surv Opr Shift Opr Support
 7. Contact: Hewitt 2 2 3294 8. Survey Date: 6/10/93 12. Task: benzene analysis
 4. Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program
 5. Name/Area/Blk: 299-WIS-82 15a. Representative of Others? Y (4)
 6. Position: BZ Source: Demo hole - well #
 7. SS#: NA
 8. Job Title: NA
 9. Resp Protect: AP AS S NA
 10. Prot Clothing: B G H C NA
 11. Cloth. Mat'l: Cotton-SWP "Whites or Anti-Cs" NA
 12. Envr Controls: X specifics: NA Break in Containment: Y
 13. Admin Controls: X specifics: NA
 14. Job Type: Other-Treatment, Storage and Disposal (TSD) Facility well analysis
 15. Freq/Duration: Work load dependent, as per TF scheduling NA
 16. Type of Sample: PM PT Area Rep. Area
 17. Inst#/Cal Date: EP 416
 18. Roto#/Cal Date: ER206 / 5/2/93
 19. Time On/Off: 1st: 09:15 / 10:20 2nd: / 3rd: /
 20. Ttl Time(min): 65 min
 21. Device/Media: Charcoal Carbotrap 300 CISA Soda Lime
 22. Media Lot #: SKC226-01.Lot: Supelco.Lot: SKC226-29.Lot: SKC226-28.Lot:
 23. Field ID#: 93- 93- 93- 93-
 24. Lab ID#: E93- E93-16-369 E93- E93-
 25. T/Press/RH: see PNL Meteorology "Hanford Surface Observation" sheet # 373-2716
 26. Flow Rate: Pre: _____ Avg: _____ Post: _____
 (L/Min) Pre: 81.3 Avg: 81.3 Post: 81.3
 27. Total Vol (L): 5.24 5/13/93
 28. Contaminant: Acetone Butanol "VOC Target List" Ammonia Hydrogen Cyanide
 29. CAS #: 67-64-1 71-36-3 "VOC Target List" 7664-41-7 74-90-8
 30. Method. Date: HAPR70-142 HAPR70-146 HAPR70-12 HAPR70-35
 31. Results. ppm: see report
 32. TWA
 33. TLV/PEL/STD: 750 ppm 50 ppm-C "VOC Target List" 25 ppm, 350ppm-S 4.7ppm-S, 10ppm-C
 34. TWA Comment: minutes of minutes reported potential exposure sampled.
 35. Spec. Activity

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 1st tube in Series
(source side) with WIS-82 93-PCR 2 Area Temp 20° RH 50%

05/10/93-SRS

D.1-45

Entered into FG By _____ Date _____
 Reviewed for FG By _____ Date _____

15.	Name/Area/Blk	WJLH # 299-015-82		15a. Representative of Others? ☒ N	
16.	Position	BZ	Source: Dowd + Coe - WJLH		
17.	SS#	NA			
18.	Job Title	NA			
19.	Resp Protect	AP	AS	S	NA
20.	Prot Clothing	B	G	H	C NA
21.	Cloth. Mat'l	Cotton-SWP "Whites or Anti-Cs"			NA
22.	Encl Controls	X	specifics: NA		Break in Containment: Y N
23.	Admin Controls	X	specifics: NA		
24.	Job Type	Other-Treatment, Storage and Disposal (TSD) Facility WJLH Analytical			
25.	Freq/Duration	Work load dependent, as per TF scheduling			
26.	Type of Sample	PH	PT	Area Rep. - Area	
27.	Inst#/Cal Date	Pump EP416			
28.	Roto#/Cal Date	ER206 15/20/93			
29.	Time On/Off	1 st : 0805 / 10:20	2 nd :	/	3 rd : /
30.	Ttl Time(min)	65 min			
31.	Device/Media	Charcoal	Carbotrap 300	CISA	Soda Lime
32.	Media Lot #	SKC226-01 lot:	Supelco lot: 454	SKC226-29 lot:	SKC226-28 lot:
33.	Field ID#	- 93-	- 93-	- 93-	- 93-
34.	Lab ID#	E93-	E93- 6 - 370	E93-	E93-
35.	T/Press/RH	see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716			
36.	Flow Rate (L/Min)	Pre: Avg	Pre: 81.3 Avg	Pre: Avg	Pre: Avg
		Post:	Post: 81.3 81.3	Post:	Post:
37.	Total Vol (L)	5.26 3/1/93			
38.	Contaminant	Acetone	Butanol	"VOC Target List"	Ammonia
39.	CAS #	67-64-1	71-36-3	"VOC Target List"	74-90-8
40.	Method. Date	HAPR70-142	HAPR70-146	HAPR70-12	HAPR70-35
41.	Results. ppm	see report			
42.	TWA				
43.	TLV/PEL/STD	750 ppm	50 ppm-C	"VOC Target List"	25 ppm, 35ppm-S 4.7ppm-S, 10ppm-C
44.	TWA Comment	minutes of minutes reported potential exposure sampled.			
45.	Spec. Activity				

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 2nd tube, in bin
(Back up) with #15-82 43 PCD1 Area Temp 70° RH 50%

HANFORD ENVIRONMENTAL
HEALTH FOUNDATION

CHAIN OF CUSTODY FORM

☒ HEHF ☐ NHS	Client/Contractor	Page <u>1</u> of <u>1</u>
	<u>WHC</u>	Customer Order No. <u>19435</u>
Client Contact <u>Philip Bentley 943-0550</u>		Sampled By <u>Same</u>
Shipped Via/By Whom <u>Same</u>		Date Shipped <u>6/10/93</u>

Laboratory Log No.	Date/ Time Sampled (UTC)	No. of Containers or Sampling Train Components	Sample ID/Type/Description	Required Analyses						Sample Storage Location
				TDU						
E93-6-369		1	W1582 PCB 93-1 Carbotrap 300	X						Fig. #10
" 370		1	W1582 PCB 93-2 Carbotrap 300	X						↓
" 371		1	W1582 PCB 93-4 (61K) Carbotrap 300	X						

Internal Sample Tracking Form Required: ☐ YES ☒ NO

	Signature	Printed Name	Company	Date	Time
Relinquished By:		PL Bentley	El Paso	6/10/93	16:00
Received By:	DA Starnu	Douglas SIMS.	HEHF	6/10/93	16:00
Relinquished By:					
Received By:					
Relinquished By:					
Received By:					
Relinquished By:					
Received By:					
Sample Condition on Receipt: <u>OK.</u>					
Additional Comments:					
Final Sample Disposition:					

Laboratory: Please document receipt of samples by signature.
Return copy of form to HEHF/NHS.
HEHF/NHS Environmental Health Sciences
805 Goethals Drive
Richland, WA 99352

Zone: Y(N) Released by: _____ Sticker: _____ 9. IH/Payroll #: Bartley/052-48-6225
Employer: WHC 2. Sample Requestor: Reddick 10. HIH Record #: _____
CO#: 100223 4. Case#: 92-0263 11. Exposure Group: (circle one)
Farm: 244 Area: E W 6. Location/Tank: 0 Surv Opr Shift Opr Support
Contact: Hewitt 3-2-5651 8. Survey Date: 6/14/93 12. Task: Soda Hile Analysis
Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

Name/Area/Blk	<u>W-11 244-W15-42</u>			15a. Representative of Others? <u>Y (1)</u>
Position	BZ	Source:	<u>Soda Hile</u>	
SS#	<u>N/A</u>			
Job Title				
Resp Protect	AP	AS	S	
Prot Clothing	B	G	H C	
Cloth. Mat'l	Cotton-SWP "Whites or Anti-Cs"			
Engr Controls	X	specifics:	Break in Containment: <u>Y</u>	
Admin Controls	X	specifics:	<u>N/A</u>	
Job Type	Other-Treatment, Storage and Disposal (TSD) Facility <u>well analyzed</u>			
Freq/Duration	Work load dependent, as per TF scheduling			
Type of Sample	FN	PT	Area Rep. <u>Area</u>	
Inst#/Cal Date	<u>Pump ET 416</u>			
Roto#/Cal Date	<u>ER 706 / 5/20/93</u>			
Time On/Off	1 st : <u>1300 / 1340</u>	2 nd :	<u>/</u>	
Ttl Time(min)	<u>40</u>			
Device/Media	Charcoal	Carbotrap 300	CISA	Soda Lime
Media Lot #	SKC226-01.Lot:	Supelco.Lot: <u>954-24</u>	SKC226-29.Lot:	SKC226-28.Lot:
Field ID#	- 93-	<u>W15-42-11-422</u>	- 93-	- 93-
Lab ID#	E93-	E93- <u>6-414</u>	E93-	E93-
T/Press/RH	see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716			
Flow Rate (L/Min)	Pre: _____	Avg: _____	Post: _____	Avg: _____
Total Vol (L)	<u>1.93</u> <u>2.47</u>			
Contaminant	Acetone	Butanol	"VOC Target List"	Ammonia
CAS #	67-64-1	71-36-3	"VOC Target List"	7664-41-7
Method. Date	HAPR70-142.	HAPR70-146.	HAPR70-12.	HAPR70-35.
Results. ppm	<u>see report</u>			
TWA				
TLV/PEL/STD	750 ppm	50 ppm-C	"VOC Target List"	25 ppm. 35ppm-S
TWA Comment	minutes of _____ minutes reported potential exposure sampled.			
Spec. Activity				

Comments: Keep tubes cool. store CT in freezer, TDU in fridge. 2nd tube in series
(Back up) with W15-42-93 PCB 5

CHAIN OF CUSTODY FORM
(continuation sheet)

☒ HEHF	Client/Contractor PC Bentley EBASCO 1201 Juddville Ave Richmond, VA 99352	Page <u>2</u> of <u>1</u>
☐ NHS		Customer Order No. 17447

[illegible]

	Signature	Printed Name	Company	Date	Time
Relinquished By:		T. C. Barthel	ETB ASCO	6/14/93	14:35
Received By:		S. Salazar	ETB ASCO	6/14/93	14:35
Relinquished By:					
Received By:					
Relinquished By:					
Received By:					
Relinquished By:					
Received By:					

Return copy of form to HEHF/NHS.

D.1-49

AF SAMPLING FORM: TFIH Organic/Inorganic

Page ____ of ____

d Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: Bentley / 152-415
 Employer: WHC 2. Sample Requestor: Rudolph 10. HIH Record #: _____
 CO#: 15923 4. Case#: 22-0200 11. Exposure Group: (circle one)
 Farm: 241 Area: E W 6. Location/Tank: 0 Surv Opr Shift Opr Support
 Contact: Hawitt 2-5000 8. Survey Date: 6/14/13 12. Task: Down Hole Analysis
 Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

Name/Area/Blk	<u>Wall 294-15-12</u>			15a. Representative of Others? <u>Y</u> (N)
1. Position	<u>PZ</u>	Source:	<u>Down Hole</u>	
2. SS#	<u>N/A</u>			
3. Job Title	<u>N/A</u>			
4. Resp Protect	<u>AP</u>	<u>AS</u>	<u>S</u>	<u>N/A</u>
5. Prot Clothing	<u>B</u>	<u>G</u>	<u>H</u>	<u>C</u> <u>N/A</u>
6. Cloth. Mat'l	<u>Cotton-SWP "Whites or Anti-Cs"</u>			<u>N/A</u>
7. Encl Controls	<u>X</u>	specifics:	<u>N/A</u> Break in Containment: <u>Y</u> <u>N</u>	
8. Admin Controls	<u>X</u>	specifics:	<u>N/A</u>	
9. Job Type	<u>Other-Treatment, Storage and Disposal (TSD) Facility wall analysis</u>			
10. Freq/Duration	<u>Work load dependent, as per TF scheduling</u>			
11. Type of Sample	<u>PH</u>	<u>PT</u>	Area Rep.	<u>Area</u>
12. Inst#/Cal Date	<u>Puma EP 406</u>			
13. Roto#/Cal Date	<u>ER 706 / 5/20/13</u>			
14. Time On/Off	1 st : <u>1300 / 1340</u>	2 nd :	<u>/</u>	3 rd : <u>/</u>
15. Ttl Time(min)				
16. Device/Media	<u>Charcoal</u>	<u>Carbotrad 300</u>	<u>CISA</u>	<u>Soda Lime</u>
17. Media Lot #	<u>SKC226-01.Lot:</u>	<u>Supelco.Lot: 890-64</u>	<u>SKC226-29.Lot</u>	<u>SKC226-28.Lot:</u>
18. Field ID#	<u>- 93-</u>	<u>W15-82-93-F155</u>	<u>- 93-</u>	<u>- 93-</u>
19. Lab ID#	<u>E93-</u>	<u>E93- 6-413</u>	<u>E93-</u>	<u>E93-</u>
20. T/Press/RH	<u>see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716</u>			
21. Flow Rate	Pre: _____ Avg	Pre: <u>44.3</u> Avg	Pre: _____ Avg	Pre: _____ Avg
(L/Min)	Post: _____	Post: <u>45.3</u>	Post: _____	Post: _____
22. Total Vol (L)	<u>25.8/1.93</u>			
23. Contaminant	<u>Acetone</u>	<u>Butanol</u>	<u>"VOC Target List"</u>	<u>Ammonia</u> <u>Hydrogen Cyanide</u>
24. CAS #	<u>67-64-1</u>	<u>71-36-3</u>	<u>"VOC Target List"</u>	<u>7664-41-7</u> <u>74-90-8</u>
25. Method. Date	<u>HAPR70-142</u>	<u>HAPR70-146</u>	<u>HAPR70-12</u>	<u>HAPR70-35</u>
26. Results. ppm	<u>see report</u>			
27. TWA				
28. TLV/PEL/STD	<u>750 ppm</u>	<u>50 ppm-C</u>	<u>"VOC Target List"</u>	<u>25 ppm, 3500m-S</u> <u>4.700m-S, 1000m-C</u>
29. TWA Comment	<u>minutes of minutes reported potential exposure sampled.</u>			
30. Spec. Activity				

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 1st tube is series
(source side) with W15-82-93 P156

EHF SAMPLING FORM: TFIH Organic/Inorganic

Page ____ of ____

Rad Zone: Y (H) Released by: _____ Sticker: _____ 9. IH/Payroll #: P.L. Bentley / 0814 6225
1. Employer: WHC 2. Sample Requestor: Rudolph 10. HIH Record #: _____
3. 13823 19447 4. Case#: 92-0290 11. Exposure Group: (circle one)
Farm: 2-1 Area: EW 6. Location/Tank: 0 Surv Opr Shift Opr Support
7. Contact: Hewitt @ 2-3081 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
14. Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

15. Name/Area/Blk GAL-028M 15a. Representative of Others? Y N

16. Position BZ Source: From TED CARB

17. SS# _____

18. Job Title _____

19. Resp Protect AP AS S

20. Prot Clothing B G H C

21. Cloth. Mat'l Cotton-SWP "Whites or Anti-Cs"

22. Engr Controls X specifics: _____ Break in Containment: Y N

23. Admin Controls X specifics: N/A

24. Job Type Other Treatment, Storage and Disposal (TSD) Facility From TED CARB

25. Freq/Duration Work load dependent, as per TF scheduling

26. Type of Sample PN PT Area Rep. N/A

27. Inst#/Cal Date BIOS model MP-2M Serial MP00300

28. Roto#/Cal Date BIOS Dry Cal Primary Standard DC-1

Time On/Off 1st: 1416 / 1420 2nd: 1 3rd: 1

30. Ttl Time(min) 4 min

31. Device/Media Charcoal Carbotrap 300 CISA Soda Lime

32. Media Lot # SKC226-01.Lot: Supelco.Lot: 554- SKC226-29.Lot: SKC226-23.Lot:

33. Field ID# 93- 28M-S 93- 93- 93-

34. Lab ID# E93- E93- 7 - 297 E93- E93-

35. T/Press/RH see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716

36. Flow Rate Pre: _____ Avg Pre: 10.4 Avg Post: 10.4 Pre: _____ Avg Post: _____

(L/Min) Post: _____

37. Total Vol 41.6 ml 3/1/93

38. Contaminant Acetone Butanol "VOC Target List" Ammonia Hydrogen Cyanide

39. CAS # 67-64-1 71-36-3 "VOC Target List" 7664-41-7 74-90-3

40. Method. Date HAPR70-142 HAPR70-146 HAPR70-12 HAPR70-35

41. Results. ppm See report

42. TWA _____

43. TLV/PEL/STD 750 ppm 50 ppm-C "VOC Target List" 25 ppm. 350ppm-S 4.700ppm-S. 100ppm-C

44. TWA Comment minutes of minutes reported potential exposure sampled.

Sec. Activity _____

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 41-205, 1st (source)

200 (210) Tube in series with 28M-S/O

CCl4 Concentration F.M. 6C-7229ppm Entered into FG By _____ Date _____

05/10/93-SRS Reviewed for FG By _____ Date _____

d Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: 7.1. 6225
 Employer: WHC 2. Sample Requestor: Rudolph 10. HIH Record #: _____
 CO#: 18323 / 7447 4. Case#: 92-0220 11. Exposure Group: (circle one)
 Farm: 241 Area: EW 6. Location/Tank: 0 Surv Op Shift Op Support
 Contact: Hewitt 2-3081 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

1. Name/Area/Blk	<u>GAC-028M</u>			15a. Representative of Others? <u>Y</u> <u>N</u>
2. Position	<u>BZ</u>	Source:	<u>From TED CARBAG</u>	
3. SS#	<u>W.H.</u>			
4. Job Title				
5. Resp Protect	<u>AP</u>	<u>AS</u>	<u>S</u>	
6. Prot Clothing	<u>B</u>	<u>G</u>	<u>H</u>	<u>C</u>
7. Cloth. Mat'l	<u>Cotton-SWP "Whites or Anti-Cs"</u>			
8. Engr Controls	<u>X</u>	specifics:		
9. Admin Controls	<u>X</u>	specifics:	<u>W.H.</u>	
10. Job Type	<u>Other Treatment, Storage and Disposal (ISU) Facility</u> <u>From TED CARBAG</u>			
11. Freq/Duration	<u>Work load dependent, as per TF scheduling</u>			
12. Type of Sample	<u>PN</u>	<u>PT</u>	<u>Area Rep.</u> <u>W.H.</u>	
13. Inst#/Cal Date	<u>Bios model MP-2M Serial MPC0300</u>			
14. Roto#/Cal Date	<u>Bios Dry Cal Primary Standard DC-1</u>			
15. Time On/Off	<u>1st: 1416</u>	<u>1420</u>	<u>2nd: /</u>	<u>3rd: /</u>
16. Ttl Time(min)	<u>4min</u>			
17. Device/Media	<u>Charcoal</u>	<u>Carbotrap 300</u>	<u>CISA</u>	<u>Soda Lime</u>
18. Media Lot #	<u>SKC226-01.Lot:</u>	<u>Supelco.Lot: 92-34</u>	<u>SKC226-29.Lot:</u>	<u>SKC226-28.Lot:</u>
19. Field ID#	<u>- 93-</u>	<u>28M-BU 93-</u>	<u>- 93-</u>	<u>- 93-</u>
20. Lab ID#	<u>E93-</u>	<u>E93- 7 - 298</u>	<u>E93-</u>	<u>E93-</u>
21. T/Press/RH	<u>see PNL Meteorology "Hanford Surface Observation" sheet # 373-2716</u>			
22. Flow Rate (L/Min)	Pre: <u>10.4</u>	Avg: <u>10.4</u>	Post: <u>10.4</u>	
23. Total Vol (L)	<u>41.6 L</u>			
24. Contaminant	<u>Acetone</u>	<u>Butanol</u>	<u>"VOC Target List"</u>	<u>Ammonia</u>
25. CAS #	<u>67-64-1</u>	<u>71-36-3</u>	<u>"VOC Target List"</u>	<u>7664-41-7</u>
26. Method, Date	<u>HAPR70-142</u>	<u>HAPR70-146</u>	<u>HAPR70-12</u>	<u>HAPR70-35</u>
27. Results, ppm	<u>See report</u>			
28. TWA				
29. TLV/PEL/STD	<u>750 ppm</u>	<u>50 ppm-C</u>	<u>"VOC Target List"</u>	<u>25 ppm, 35ppm-S</u>
30. TWA Comment	<u>minutes of minutes reported potential exposure sampled.</u>			
31. Spec. Activity				

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 1st 2nd 1st (source)

d Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: Bentley / 0225
 1. Employer: WHC 2. Sample Requestor: Rudolph 10. HIH Record #: _____
 3. 18923 19417 4. Case#: 92-0280 11. Exposure Group: (circle one)
 Farm: 241 Area: E(W) 6. Location/Tank: 0 Surv Opr Shift Opr Support
 Contact: Hewitt 3 2-3081 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

1. Name/Area/Blk	GAC-29B		15a. Representative of Others?	Y ☒ N ☐
2. Position	BZ	Source:	From TED CARBAC	
3. SS#	N/A			
4. Job Title				
5. Resp Protect	AP AS S			
6. Prot Clothing	B G H C			
7. Cloth. Mat'l	Cotton-SWP "Whites or Anti-Cs"			
8. Engr Controls	X	specifics:	Break in Containment: Y ☐ N ☒	
9. Admin Controls	X	specifics:	N/A	
10. Job Type	<u>Other Treatment, Storage and Disposal (TSU) Facility</u> From TED CARBAC			
11. Freq/Duration	Work load dependent, as per TF scheduling			
12. Type of Sample	PN PT	Area Rep.	N/A	
13. Inst#/Cal Date	Bios model MP-24 Serial MP00300			
14. Roto#/Cal Date	Bios Dry Cal Primary Standard DC-1			
15. e On/Off	1": 1433 / 1436	2": /	3": /	
16. Int'l Time(min)	3			
17. Device/Media	Charcoal	Carbotrap 300	CISA	Soda Lime
18. Media Lot #	SKC226-01.Lot:	Supelco.Lot: 954-27	SKC226-29.Lot:	SKC226-28.Lot:
19. Field ID#	- 93-	29B-S 93-	- 93-	- 93-
20. Lab ID#	E93-	E93-7-299	E93-	E93-
21. T/Press/RH	see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716			
22. Flow Rate (L/Min)	Pre: Avg	Pre: 10.4 Avg	Pre: Avg	Pre: Avg
	Post:	Post: 10.4 10.4	Post:	Post:
23. Total Vol (L)	31.2 ml 7/1/93			
24. Contaminant	Acetone Butanol	"VOC Target List"	Ammonia	Hydrogen Cyanide
25. CAS #	67-64-1 71-36-3	"VOC Target List"	7664-41-7	74-90-8
26. Method. Date	HAPR70-142	HAPR70-146	HAPR70-12	HAPR70-35
27. Results. ppm	see report			
28. TWA				
29. TLV/PEL/STD	750 ppm 50 ppm-C	"VOC Target List"	25 ppm, 3500m-S	4.700m-S, 1000m-C
30. TWA Comment	minutes of minutes reported potential exposure sampled.			
31. Activity				

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 41 tubes 1st Source

200 (3/10) Tube in series with 29B-B/L
 CCC4 concn. on Field GC - 9,000 ppm

05/10/93-SRS

Entered into FG By _____ Date _____
 Reviewed for FG By _____ Date _____

D.1-53

Zone: Y (11) Released by: _____ Sticker: _____ 9. IH/Payroll #: 6225
 Employer: WHC 2. Sample Requestor: Radon 10. HIH Record #: _____
 CO#: 10000 4. Case#: 62-6225 11. Exposure Group: (circle one)
 Farm: 241 Area: EW 6. Location/Tank: 0 Surv Cpr Shift Cpr Support
 Contact: Hawitt 3-2-3091 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

Name/Area/Blk	<u>GAC-29B</u>		15a. Representative of Others?	<u>Y</u> <u>N</u>
Position	<u>BZ</u>	Source:	<u>From TED CARBAC</u>	
SS#	<u>W/L</u>			
Job Title				
Resp Protect	<u>AP</u>	<u>AS</u>	<u>S</u>	
Prot Clothing	<u>B</u>	<u>G</u>	<u>H</u>	<u>C</u>
Cloth. Mat'l	<u>Cotton-SWP "Whites or Anti-Cs"</u>			
Engr Controls	<u>X</u>	specifics:	<u>Break in Containment: Y N</u>	
Admin Controls	<u>X</u>	specifics:	<u>W/L</u>	
Job Type	<u>Other Treatment, Storage and Disposal (ISU) Facility</u> <u>From TED CARBAC</u>			
Freq/Duration	<u>Work load dependent, as per TF scheduling</u>			
Type of Sample	<u>PN</u>	<u>PT</u>	<u>Area Rep.</u> <u>W/L</u>	
Inst#/Cal Date	<u>BIOS model MP-2M Serial MP00300</u>			
Roto#/Cal Date	<u>BIOS Dry Cal Primary Standard DC-1</u>			
Time On/Off	<u>1st: 1433 / 1436</u>	<u>2nd: /</u>	<u>3rd: /</u>	
Ttl Time(min)	<u>3</u>			
Device/Media	<u>Charcoal</u>	<u>Carbotrap 300</u>	<u>CISA</u>	<u>Soda Lime</u>
Media Lot #	<u>SKC226-01.Lot:</u>	<u>Supelco.Lot: 32</u>	<u>SKC226-29.Lot:</u>	<u>SKC226-28.Lot:</u>
Field ID#	<u>- 93-</u>	<u>29B-B/L 93-</u>	<u>- 93-</u>	<u>- 93-</u>
Lab ID#	<u>E93-</u>	<u>E93- 7 - 300</u>	<u>E93-</u>	<u>E93-</u>
T/Press/RH	<u>see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2715</u>			
Flow Rate (L/Min)	Pre: _____ Avg _____	Pre: <u>10.4</u> Avg <u>10.4</u>	Pre: _____ Avg _____	Pre: _____ Avg _____
	Post: _____	Post: <u>10.4</u>	Post: _____	Post: _____
Total Vol <u>ml</u>	<u>31.2 ml</u> <u>8/17/93</u>			
Contaminant	<u>Acetone</u>	<u>Butanol</u>	<u>"VOC Target List"</u>	<u>Ammonia</u>
CAS #	<u>67-64-1</u>	<u>71-36-3</u>	<u>"VOC Target List"</u>	<u>7664-41-7</u>
Method. Date	<u>HAPR70-142</u>	<u>HAPR70-146</u>	<u>HAPR70-12</u>	<u>HAPR70-35</u>
Results. ppm	<u>see report</u>			
TWA				
TLV/PEL/STD	<u>750 ppm</u>	<u>50 ppm-C</u>	<u>"VOC Target List"</u>	<u>25 ppm, 35ppm-S</u>
TWA Comment	<u>minutes of minutes reported potential exposure sampled.</u>			
Spec. Activity				

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 1st tube 1st (source)

2nd (B/L) tube in series with 29B-5

5/10/93-SRS CLL4 conc. on R/LB GC - 9,000 ppm Entered into FG By _____ Date _____
 Reviewed for FG By _____ Date _____

HF SAMPLING FORM: TFIH Organic/Inorganic

Code

Page ____ of ____

1. Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: 6225
 2. Sample Requestor: Rudolph 10. HIH Record #: _____
 3. Case #: 92-0200 11. Exposure Group: (circle one)
 4. Location/Tank: 0 Surv Opr Shift Opr Support
 5. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 6. Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

13. Name/Area/Blk GAC-25T 15a. Representative of Others? Y N

14. Position BZ Source: From TED C2B4

15. SS# _____

16. Job Title _____

17. Resp Protect AP AS S

18. Prot Clothing B G H C

19. Cloth. Mat'l Cotton-SWP "Whites or Anti-Cs"

20. Envr Controls X specifics: _____ Break in Containment: X

21. Admin Controls X specifics: _____

22. Job Type Other Treatment, Storage and Disposal (TSD) Facility From TED C2B4

23. Freq/Duration Work load dependent, as per TF scheduling

24. Type of Sample PN PT Area Rep. NH

25. Inst#/Cal Date BIOS model MP-2m Serial MP00300

26. Roto#/Cal Date BIOS Dry Cal Primary Standard DC-1

27. On/Off 1": 1442 / 1445 2": / 3": /

28. Ttl Time(min) 3

29. Device/Media Charcoal Carbotrap 300 CISA Soda Lime

30. Media Lot # SKC226-01.Lot: Supelco.Lot: SKC226-29.Lot SKC226-23.Lot:

31. Field ID# 93- 25T-S 93- 93- 93-

32. Lab ID# E93- E93- 7 - 301 E93- E93-

33. T/Press/RH see PNL Meteorology "Hanford Surface Observation" sheet 3 373-2716

34. Flow Rate Pre: _____ Avg Pre: 10.4 Avg Post: _____ Avg

35. (L/Min) Post: _____ Post: 10.4 Post: _____ Post: _____

36. Total Vol 31.2 ml 8/1/93

37. Contaminant Acetone Butanol "VOC Target List" Ammonia Hydrogen Cyanide

38. CAS # 67-64-1 71-36-3 "VOC Target List" 7664-41-7 74-90-8

39. Method, Date HAPR70-142 HAPR70-146 HAPR70-12 HAPR70-35

40. Results, ppm see report

41. TWA _____

42. TLV/PEL/STD 750 ppm 50 ppm-C "VOC Target List" 25 ppm, 3500m-S 4.700m-S, 1000m-C

43. TWA Comment minutes of minutes reported potential exposure sampled.

44. Activity _____

45. Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 41-206 T (st source)

Tube in series with 25T-B/C

CLL4 conc. on Field GC 48 ppm

05/10/93-SRS Entered into FG By _____ Date _____

Reviewed for FG By _____ Date _____

AF SAMPLING FORM: TFIH Organic/Inorganic

Page ____ of ____

1. Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: 6225
 Employer: WHC 2. Sample Requestor: Fudon 10. HIH Record #: _____
 CO#: 18922 / 19447 4. Case#: 92-0200 11. Exposure Group: (circle one)
 Farm: 241 Area: EW 6. Location/Tank: _____ 0 Surv. Opr. Shift Opr. Support
 Contact: Hewitt 2-3081 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 Survey Title: Funk Farm Industrial Hygiene (TFIH) Evaluation Program

Name/Area/Blk GAC-25T 15a. Representative of Others? Y II

Position BZ Source: From TED LAB

SS# _____

Job Title _____

Resp Protect AP AS S

Prot Clothing B G H C

Cloth. Mat'l Cotton-SWP "Whites or Anti-Cs"

Encl Controls X specifics: _____ Break in Containment: Y N

Admin Controls X specifics: _____

Job Type Other Treatment, Storage and Disposal (ISU) Facility From TED Lab

Freq/Duration Work load dependent, as per TF scheduling

Type of Sample PH PT Area Rep. NH

Inst#/Cal Date BIOS model MP-24 Serial MP00300

Roto#/Cal Date BIOS Dry Cal Primary Standard DC-1

Time On/Off 1st: 1442 / 1445 2nd: 1 3rd: 1

Ttl Time(min) 3

1. Device/Media Charcoal Carbotrap 300 CISA Soda Lime

2. Media Lot # SKC226-01.Lot: Sudelco.Lot: 954-32 SKC226-29.Lot SKC226-28.Lot:

3. Field ID# - 93- 25T-B/U 93- - 93- - 93-

4. Lab ID# E93- E93- 7-302 E93- E93-

5. T/Press/RH see PNL Meteorology "Hanford Surface Observation" sheet @ 373-2716

6. Flow Rate Pre: _____ Avg _____ Post: _____

(L/Min) Pre: 10.4 Avg 10.4 Post: 10.4

7. Total Vol 31.2 ml 4/7/93

8. Contaminant Acetone Butanol "VOC Target List" Ammonia Hydrogen Cyanide

9. CAS # 67-64-1 71-36-3 "VOC Target List" 7664-41-7 74-90-8

10. Method. Date HAPR70-142 HAPR70-146 HAPR70-12 HAPR70-35

1. Results. ppm See report

2. TWA _____

3. TLV/PEL/STD 750 ppm 50 ppm-C "VOC Target List" 25 ppm, 35ppm-S 4.7ppm-S, 10ppm-C

4. TWA Comment minutes of minutes reported potential exposure sampled.

5. Spec. Activity _____

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 4st 200, 1st (Source)

200 (BU) Tube in series with 25T-S

5/10/93-SRS Entered into FG By _____ Date _____

d Zone: Y (N) Released by: _____ Sticker: _____ 9. IH/Payroll #: _____
 F. Employer: WHC 2. Sample Requestor: Rudolph 10. HIH Record #: _____
 18923 14407 4. Case#: 92-0200 11. Exposure Group: (circle one)
 241 Area: E(W) 6. Location/Tank: 0 Surv Cpr Shift Cpr Support
 Contact: Hewitt 2-3081 8. Survey Date: 7/1/93 12. Task: Analysis of GAC Description
 Survey Title: Tank Farm Industrial Hygiene (TFIH) Evaluation Program

1. Name/Area/Blk BLANK 15a. Representative of Others? Y N

2. Position BZ Source: FROM TED LARBAK

3. SS# _____

4. Job Title _____

5. Resp Protect AP AS S

6. Prot Clothing B G H C

7. Cloth. Mat'l Cotton-SWP "Whites or Anti-Cs"

8. Engr Controls X specifics: _____ Break in Containment: Y N

9. Admin Controls X specifics: (1)

10. Job Type Other Treatment, Storage and Disposal (TSU) Facility FROM TED LARBAK

11. Freq/Duration Work load dependent, as per TF scheduling

12. Type of Sample PM PT Area Rep. 1h

13. Inst#/Cal Date BIOS model MP-24 Serial MP00300

14. Roto#/Cal Date BIOS Dry Cal Primary Standard DC-1

15. e On/Off 1": 1 2": 1 3": 1

16. Fil Time(min) 0

17. Device/Media Charcoal Carbotrap 300 CISA Soda Lime

18. Media Lot # SKC226-01, Lot: Supelco, Lot: 813-11 SKC226-29, Lot: SKC226-28, Lot:

19. Field ID# 93- BLANK 93- 93- 93-

20. Lab ID# E93- E93-7-303 E93- E93-

21. T/Press/RH see PNL Meteorology "Hanford Surface Observation" sheet 3 373-2716

22. Flow Rate (L/Min) Pre: _____ Avg: _____ Post: _____ Avg: _____ Pre: _____ Avg: _____ Post: _____ Avg: _____

23. Total Vol (L) blank 8/1/93

24. Contaminant Acetone Butanol "VOC Target List" Ammonia Hydrogen Cyanide

25. CAS # 67-64-1 71-36-3 "VOC Target List" 7664-41-7 74-90-8

26. Method, Date HAPR70-142 HAPR70-146 HAPR70-12 HAPR70-35

27. Results, ppm See report

28. TWA _____

29. TLV/PEL/STD 750 ppm 50 ppm-C "VOC Target List" 25 ppm, 35ppm-S 4.7ppm-S, 10ppm-C

30. TWA Comment minutes of minutes reported potential exposure sampled.

31. c. Activity _____

Comments: Keep tubes cool, store CT in freezer, TDU in fridge. 4st 206 - 1st 300

206 (30) Tubes in serial with BLANK

Entered into FG By _____ Date _____
 Reviewed for FG By _____ Date _____

05/10/93-SRS D.1-57

HANFORD ENVIRONMENTAL
HEALTH FOUNDATION

CHAIN OF CUSTODY FORM

☒ HEHF ☐ NHS	Client/Contractor ERBSCO - WHC PINE BLUFF KIDN-SWETT, WAC	Page <u>1</u> of <u>1</u> Customer Order No. <u>19447</u>
	Client Contact <u>RAHLEY</u> Shipped Via/By Whom <u>ERBSCO ? / HEHF - SIMONS</u>	Sampled By <u>Rahley - ERBSCO</u> Date Shipped ? <u>07-13-93</u>

Laboratory Log No.	Date/ Time Sampled	No. of Containers or Sampling Train Components	Sample ID/Type/Description	Required Analyses						Sample Storage Location
				TDH						
93-7-297	10-10-1993	1	25M-S	1						Reling.
298	+	1	28M-B/U							
299	10-13-1993	1	29B-S							
300	+	1	29B-B/U							
301	10-13-1993	1	25T-S							
302	+	1	25T-B/U							
303	-	1	PLANK	↓						↓

Internal Sample Tracking Form Required: ☐ YES ☒ NO

	Signature	Printed Name	Company	Date	Time
Relinquished By:	(4)				
Received By:	S.R. Simons	S.R. Simons	HEHF	07-12-93	10:5
Relinquished By:	S.R. Simons	S.R. Simons	HEHF	07-13-93	10:51
Received By:	S. Salazar	S. Salazar	HEHF	7/13/93	10:51
Relinquished By:					
Received By:					
Relinquished By:					
Received By:					
Sample Condition on Receipt: <u>OK</u>					
Additional Comments: <u>(4) NO C-O-C initiated by ERBSCO, Picked up by Sam P. Smith Brian P. L.</u>					
<u>ERBSCO on 07-12-93 @ 10:15</u>					
Final Sample Disposition:					

Laboratory: Please document receipt of samples by signature.

Return copy of form to HEHF/NHS.

HEHF/NHS Environmental Health Sciences

805 Goethals Drive

Richland, WA 99352

ATTACHMENT D.1-2

The following is a list of organic compounds found by HEHF from well 299-W15-82 as a result of analyzing TDU tube samples taken at a depth of 98.5 ft on June 10, 1993.

Acetonitrile
n-Hexane
Methyl Ethyl Ketone
Carbon Tetrachloride
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene
2-Hexanone
Ethyl Benzene
p-Xylene
o-Xylene
Chloroform
Octane
Decane
Hexachloroethane
Other unidentified C-10 hydrocarbons
3-Methyl Pentane
Methylene Chloride
Methylcyclopentane
3-Methyl Heptane
2-Butene
Pentadiene
2-methyl-2-propanol
2-methyl-2-propanal
4-hydroxy-4-methyl-2-pentanone
a-pinene
cyclohexanone
D-Limonene
phenol
trimethyl or methyl ethyl benzene

Acetone and acetonitrile were observed but not positively identified.
Higher boiling point compounds observed but peaks unresolved.

ATTACHMENT D.1-3

The following is a list of organic compounds found by HEHF from Well 299-W15-82 as a result of analyzing TDU tube samples taken at a depth of 65 ft on June 14, 1993.

Chloroform
Carbon Tetrachloride
Acetic Acid
1,1,1, - Trichloropropane
Tetrachloroethylene
Hexachloroethane
Napthalene or Azulene
Hydrochloric Acid (high background reading)

Analysis was shut down several times due to high carbon tetrachloride concentrations.

ATTACHMENT D.1-4
INORGANIC ANALYSES OF OVERHEATED GAC

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone (509) 376-3353

June 16, 1993

RECEIVED

P.L. Bartley
EBASCO ENVIRONMENTAL
1201 Jadwin Ave, Suite 202
Richland, Washington

JUN 17 1993
EBASCO - RICHLAND

Dear Phil

The gas sample analysis on your sample [TWO] is complete. The WHC work order number is ED3731. The mass spectrometer used is a Finnigan MAT-271 that is calibrated on a monthly basis. Nitrogen is run each day the instrument is used.

The results are attached to this letter.

If you have any questions please contact me.

Sincerely

A handwritten signature in dark ink, appearing to read "Milton W. Goheen".

Milton W Goheen
Atomic and Molecular Spectroscopy

A handwritten signature in dark ink, appearing to read "John E. Curran".
Concurrence

MASS SPECTROMETER LABORATORIES P7-22 325 BUILDING 300 AREA

TO: P.L.Bartley

LRB Number: 54411
M&TE Number: WC83625

Page Number: 64
METHOD PNL-MA-ALO-284

MASS SPECTROMETRIC GAS ANALYSIS [Mole %]

ANALYST: MW Goheen *[Signature]* DATE ANALYZED: 6-14-93
REVIEWED BY: JH Ennen *[Signature]* DATE: 6-16-93

CUSTOMER I.D.: TWO ALO LOG-IN NUMBER: 93-07957 OSN: 21124

H ₂	<0.0007	±	
³ He	<0.001	±	
⁴ He	<0.001	±	
CH ₄	<0.001	±	
N ₂	78.1	±	0.2
CO	0.003	±	0.001
O ₂	20.7	±	0.2
Ar	0.928	±	0.009
CO ₂	0.206	±	0.003
N ₂ O	<0.001	±	
NO _x	<0.001	±

Battelle

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone 509/

376-3353

July 8, 1993

RECEIVED

JUL 12 1993

EBASCO-RICHLAND

Brian Peters/P.L.Bartley
EBASCO Environmental
1201 Jadwin Ave, Suite 202
Richland, Washington

Dear Brian,

Analyses on three gas samples are complete. Phil delivered the samples to the 325 building mass spectrometer lab on 7-2-93. The WHC work order number for the analyses is ED3731. The mass spectrometer used is a Finnigan MAT-271. Calibration is done on a monthly basis. A nitrogen sensitivity check is run each day the instrument is used.

The results are included with this letter. If you have any questions please contact me.

Sincerely,

Milton W Goheen
Atomic and Molecular Spectroscopy

Concurrence: *R E Gorman*

Pacific Northwest Laboratory

From: Inorganic Mass Spectrometry Lab.
 Phone: (509) 376-3358 / mail slot P7-22
 Date: July 7, 1993
 Subject: Gas Species Analysis

To: P.L. Bartley

Analytical procedure: PNL-MA-299 ALO-284
 Laboratory record book 54411 Page 71
 Measurement and test equipment WC38625

Sample Id.	29B		
Analysis Date	July 7, 1993	Mole	Estimate
Log-in No.	93-08641	Percent	of Precision
Argon		0.08 ±	0.02
Carbon dioxide		0.06 ±	0.02
Carbon monoxide		<0.05 ±	
Helium		91.8 ±	0.1
Hydrogen		<0.001 ±	
Methane		<0.001 ±	
Nitrogen		6.35 ±	0.07
Oxygen		1.73 ±	0.03
Nitrous oxide		<0.001 ±	
Other nitrogen oxides		<0.001 ±	
Comments	CCl4 is major contaminate		

Sample Id.	28M		
Analysis Date	July 7, 1993	Mole	Estimate
Log-in No.	93-08642	Percent	of Precision
Argon		0.084 ±	0.004
Carbon dioxide		0.018 ±	0.004
Carbon monoxide		<0.05 ±	
Helium		91 ±	0.1
Hydrogen		0.0007 ±	0.0002
Methane		<0.0005 ±	
Nitrogen		6.96 ±	0.08
Oxygen		1.92 ±	0.03
Nitrous oxide		<0.001 ±	
Other nitrogen oxides		<0.001 ±	
Comments	CCl4 is minor contaminate		

Pacific Northwest Laboratory

From: Inorganic Mass Spectrometry Lab.
 Phone: (509) 376-3358 / mail slot P7-22
 Date: July 7, 1993
 Subject: Gas Species Analysis

To: P.L. Bartley

Analytical procedure: PNL-MA-299 ALO-284
 Laboratory record book 54411 Page 71
 Measurement and test equipment WC38625

Sample Id.	25T		Estimate
Analysis Date	July 7, 1993	Mole	of
Log-in No.	93-08643	Percent	Precision
Argon		0.27	= 0.04
Carbon dioxide		<0.05	=
Carbon monoxide		<0.05	=
Helium		70.8	= 0.1
Hydrogen		0.033	= 0.003
Methane		0.001	= 0.0005
Nitrogen		22.8	= 0.3
Oxygen		6.06	= 0.06
Nitrous oxide		0.043	= 0.001
Other nitrogen oxides		<0.001	=
Comments			

ATTACHMENT D.2

THERMOGRAVIMETRIC ANALYSIS OF GRANULAR ACTIVATED CARBON
AND CARBON TETRACHLORIDE

D.2.1.0 INTRODUCTION

In response to the overheating incident that took place at the 216-Z-9 Trench on June 3, 1993, a series of thermogravimetric studies were performed on granular activated carbon (GAC). The following sections of this report describe the tests that were performed, the results obtained, and recommendations for further tests.

D.2.2.0 TEST DESCRIPTION

Three tests were performed to determine the sorption, desorption, and thermal stability of GAC with and without the presence of carbon tetrachloride. The instruments and tests are described below.

D.2.2.1 INSTRUMENT DESCRIPTION

These tests were performed by G.S. Barney of WHC's Plutonium Process Support Laboratory using a thermogravimetric analyzer and mass spectrometer (TGA/MS). In simple terms, the TGA is an very sensitive scale placed inside of an oven. The oven temperature can be precisely controlled and the sample weight loss or gain monitored. The TGA also has a differential temperature analyzer (DTA) that measures the temperature difference between the sample and the oven. The DTA thus allows the determination of endothermic and exothermic properties of the sample. The endothermic/exothermic scale is generally only qualitative. With appropriate standards it may be possible to quantify the energy; however, this has currently not been done.

The TGA oven and sample chamber are coupled to an MS. A carrier gas is swept past the sample and flushed into the MS for analysis. The MS ionizes the sample gases and determines the mass of the ionized particles by a method analogous to the prism or grating in an optical spectrometer. The ionizing source will generally break a sample compound into fragments. For example, the primary mass peaks for carbon tetrachloride are 117, 118, 119, and 120 mass units (m.u.). These correspond to the CCl_3 ion with various combinations of the ^{35}Cl and ^{36}Cl atoms. An initial list of compounds of interest and the primary mass peaks is given in Table D.2-1.

D.2.2.2 TEST DESCRIPTIONS

Three tests were performed. The first test used only virgin GAC to establish a baseline for comparison. For purposes of this report, "virgin" GAC refers to GAC that has not been previously exposed to carbon tetrachloride. The second test repeated the first test using carbon tetrachloride-saturated GAC to monitor the desorption process. The third test repeated the first test with virgin GAC, but with a sweep gas containing 60% relative humidity (RH) and 30,000 ppm, of carbon tetrachloride to estimate the heat of adsorption and monitor the adsorption process.

Table D.2-1. Mass Spectrometer Compounds of interest.

Compound	Primary mass units
Water	18
Oxygen	32
Chlorine	35,36
Argon	40
Carbon dioxide	44
Phosgene	63, 64 ^a
Carbon tetrachloride	117, 118, 119, 120

^aThe mass unit for phosgene is assumed to be 63 and 64. A reference spectrograph for phosgene was not yet available.

D.2.2.2.1 Baseline Test

The first test used only virgin GAC removed from one of the unused VES canisters to establish a baseline from which subsequent tests could be compared. A sample of the GAC was placed in the TGA/MS instrument and heated from 77 °F to 860 °F at a rate of 5.5 °F/min. The sample carrier gas was dry air.

D.2.2.2.2 Desorption Test

For this test, some virgin GAC was placed in a column and an air stream containing 3,000 ppm_v of carbon tetrachloride was passed through it overnight. A sample of this saturated GAC was then tested using the same conditions as the baseline test.

D.2.2.3 Adsorption Test

Virgin GAC was used for this test also, but the sample carrier gas was changed to an air stream containing 60% RH and 30,000 ppm_v of carbon tetrachloride. This test was performed in two stages: for the first, the temperature was maintained at 77 °F for 2 h; during the second stage the temperature was increased to 860 °F at a rate of 5.5 °F/min. The first stage allowed for gathering data on the heat of adsorption at 77 °F. The second stage was to simulate the operating conditions present during the canister overheating incident.

D.2.3.0 TEST RESULTS

The results for the three tests (baseline, desorption, and adsorption) are given in the following sections. The graphs that correspond to these test

results were done at WSU and are in units of degrees Celcius. The temperatures in this section that refer to these graphs have been converted to degrees Celcius and appear in parentheses behind the Fahrenheit units for ease of comparison.

D.2.3.1 BASELINE TEST

Results from the baseline test are shown in Figures D.2-1, D.2-2, D.2-3, and D.2-4. The main information of note from these figures is that oxidation of the GAC begins at 480 °F (249 °C) and becomes significant over 570 °F (299 °C). There seems to be an anomaly in the DTA curve (Figure D.2-1) at 680 °F (360 °C) where the exothermic reaction appears to slow down for approximately 55 °F (13 °C) (10 min) and then takes off again at a greatly accelerated rate. Figure D.2-2 shows that the water and oxygen initially on the GAC are relatively quickly desorbed. The oxygen concentration decreases slightly starting at 480 °F (249 °C), which corresponds with oxidation of the GAC. The evolution of carbon dioxide is shown in Figure D.2-3. As expected, the carbon dioxide concentration greatly increases at the temperature corresponding to GAC oxidation. Figure D.2-4 shows the argon concentration during the test. Argon is normally used as the sample carrier gas during operation of the TGA/MS instrument. The elevated concentrations early in the test run indicate that the sample chamber was not fully flushed prior to beginning this test.

D.2.3.2 DESORPTION TEST

Results from the desorption test are shown in Figures D.2-5, D.2-6, D.2-7, D.2-8, D.2-9, and D.2-10. Figure D.2-5 shows that the adsorbed carbon tetrachloride desorbs at a nearly linear rate over the temperature range of 77 °F to 540 °F (25 °C to 282 °C). The DTA curve indicates that an exothermic reaction begins at approximately 300 °F (149 °C) and stops by the time the temperature reaches 630 °F (332 °C) (elapsed time of 1 h). A second exotherm then occurs, which presumably corresponds to GAC oxidation. If the second exotherm does indicate the onset of GAC oxidation, this represents an increase in the GAC oxidation temperature of approximately 140 °F (60 °C) due to the presence of carbon tetrachloride.

Additional analysis of the MS data will be required to determine if the products of the initial exothermic reaction can be identified. This analysis was not available in time for this report.

The relative concentrations of carbon tetrachloride and water compared with the TG and DTA traces are shown in Figures D.2-6 and D.2-7, respectively. These figures show that the rate of desorption of carbon tetrachloride increased with temperature reaching a maximum at 320 °F (160 °C). This behavior is likely to be a result of desorbing a majority of the carbon tetrachloride rather than an effect of increasing temperature. The water concentration, however, decreased at a constant rate. The mass spectrographs at 170 °F, 240 °F, and 410 °F (77 °C, 116 °C, and 210 °C) are given in Figures D.2-8, D.2-9, and D.2-10, respectively.

D.2.3.3 ADSORPTION TEST

Results from the adsorption test are given in Figures D.2-11, D.2-12, D.2-13, D.2-14, and D.2-15. Figure D.2-11 shows that during the 2 h of operation at 77 °F (25 °C), the GAC adsorbed 10 wt% of carbon tetrachloride. The DTA curve shown in Figure D.2-12 indicates that the heat of adsorption of carbon tetrachloride decreased with increased loading on the GAC. No attempt was made to quantify this heat of adsorption for this initial test. Quantification requires a standard with a known heat of reaction be used to calibrate the DTA.

Figure D.2-13 shows that in addition to the 10 wt% of carbon tetrachloride, the GAC also contained 2 wt% of some other volatile, which is presumably water. In general, the DTA curve of the sample during heating is similar to that seen in the desorption test. That is, a broad exotherm occurs from 210 °F to 540 °F (99 °C to 282 °C) and then disappears followed by oxidation of the carbon at 660 °F to 750 °F (349 °C to 399 °C). The scale for the DTA trace in this figure has not been adjusted (baselined) to place the zero in the correct location. This figure will be revised in a subsequent revision.

Figures D.2-14 and D.2-15 show the concentrations of compounds with the mass units 117, 18, 44, 35, 36, and 63. There are two things to note in these figures. The first is that the concentrations of everything except carbon dioxide (m.u. 44) drop at 200 min into the test. This occurred when the air flow to the system momentarily failed. The second item is that phosgene (m.u. 63) has a constant concentration throughout the test run. It is not reasonable that phosgene is present even at ambient temperatures. A possible explanation is that phosgene is formed within the MS during the ionization process.

D.2.4.0 CONCLUSIONS AND RECOMMENDATIONS

Significant conclusions from this testing include the following.

- Significant oxidation of virgin GAC starts at 480 °F (249 °C).
- The presence of adsorbed carbon tetrachloride increases the temperature at which GAC oxidation occurs.
- It appears that an exothermic reaction begins at approximately 300 °F (149 °C) when carbon tetrachloride is present.
- The carbon tetrachloride heat of adsorption decreases as the GAC saturation increases.

It is recommended that two replicates of each of the three tests be performed. This will help determine if the tests are reproducible and may provide insight into the unknown exothermic reaction and the variable slope of the GAC oxidation exotherm. More detailed analysis of the mass spectrographs should also be performed. The DTA should also be standardized to allow quantification of the heat of adsorption during replication of the adsorption tests.

Figure D.2-1. Baseline Test, TG and DTA Traces.

09/30/93

D.2-8

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Figure D.2-2. Baseline test, TG, Water (m.u. 18), and Oxygen (m.u. 32) Traces.

Figure D.2-3. Baseline Test, TG and Carbon Dioxide (m.u. 44) Traces.

09/30/93

D.2-10

WHC-SD-EN-TI-203, Rev. 0

Figure D.2-4. Baseline Test, TG and Argon (m.u. 40) Traces.

Figure D.2-5. Desorption Test, TG and DTA Traces.

Figure 0.2-6. Desorption test, 16, DIA, and Carbon tetrachloride (m.u. 117) Traces.

Figure D.2-7. Description test, IG, DIA, and Water (m.u. 1B) traces.

09/30/93

D.2-14

Figure D.2-8. Desorption Test, Mass Spectrograph at 77 °F.

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IDENTITY No.	GAC W/CCL4 = H2	SAMPLE	3000 PPMV	143.80 mg	TG	250 mg	~
DATE	29 Jul 1993	REFERENCE	MT	0.00 mg	DTA	500 uV	
OPERATOR	GSD	ATMOSPHERE	AIR	/ 100			
LABORATORY	PPSL	CRUCIBLE	PT	Sog. 1: 20°C/ 5.00/ 500 °C			

Figure D.2-9. Desorption Test, Mass Spectrograph at 117 °C.

09/30/93

D.2-16

Figure D.2-10. Desorption Test, Mass Spectrograph at 208 °C.

WHC-SD-EN-TI-203, Rev. 0

09/30/93

D.2-17

NETZSCH S T R - Q M S - System: 409/429-403

IDENTITY No.	CCL4 ADS ON GAC	SAMPLE	GAC	105.00 mg	TG	250 mg	TGc2
DATE	5 Aug 1993	REFERENCE	HT	0.00 mg	DTA	500 uV	Bas
OPERATOR	CSB	ATMOSPHERE	HR	100			
LABORATORY	PPSL	CRUCIBLE	PT				
				Seg. 2: 30°C/ 2.00/ 30 °C			

Figure D.2-11. Adsorption Test, TG and Temperature Traces.

WHC-SD-EN-TI-203, Rev. 0

09/30/93

D.2-18

WMC-SD-EN-TI-203, Rev. 0

Figure D.2-12. Adsorption Test, DTA and Temperature Traces.

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4 of 6

Figure D.2-13. Adsorption Test, TG and DTA Traces.

09/30/93

D.2-20

Figure D.2-14. Adsorption Test, Temperature and Carbon Tetrachloride
(m.u. 117) Traces.

09/30/93

D.2-21

Figure D.2-15. Adsorption Test, TG, Temperature, Water (m.u. 18), Carbon Dioxide (m.u. 44), Chlorine (m.u. 35, 36), and Phosgene (m.u. 63) Traces.51

ATTACHMENT D.3

ANALYSIS OF FIRST FULL-SCALE THERMOCOUPLE RESPONSE TEST
JUNE 28, 1993

ATTACHMENT D.3
ANALYSIS OF FIRST FULL-SCALE THERMOCOUPLE RESPONSE TEST
JUNE 28, 1993

Thermocouple instrumentation of the GAC-filled canister appears to be an appropriate tool for monitoring the temperature trends within the carbon bed. A temperature wave was detected in this simple test of passing heated air through the carbon bed. Therefore, it seems likely that a temperature wave produced by heat released from heat of adsorption will similarly be detectable as a result of a mass wave moving through the bed.

Observations and comments based on an analysis of the temperature profiles generated during the test are given at the end of this report. What follows here is an explanation of the quantifiable aspects of the test.

AIR FLOW AND HEAT INPUT CALCULATIONS

The heated air flow through the canister was analyzed and the net total heat input from the heated air stream was calculated. These calculations are shown in Tables D.3-1 and D.3-2. In all cases temperatures were assumed to be uniform in the horizontal plane. Based on measured air flow and temperatures, approximately 68,000 Btu were put into the GAC system by the air stream during the 7 h 20 minute test period. The GAC system includes the carbon bed (the GAC), water in the GAC, the metal canister, and losses from the canister.

HEAT FLOW WITHIN GAC SYSTEM

The total net heat input to the GAC system by the air stream was distributed to a number of heat sinks. The bulk of the heat went to desorbing GAC moisture or was absorbed by the GAC itself. Smaller, but potentially significant quantities of heat can be absorbed or lost and have a significant impact on results. This analysis characterizes the approximate relative magnitudes of these heat quantities.

The ultimate sinks or losses of heat in the GAC system are listed below:

- Absorbed by the GAC
- Used to desorb water vapor from the GAC
- Absorbed by the metal canister
- Losses from airspace above the GAC
- Lost through the wall of the canister.

The following analysis attempts to characterize the magnitudes of these potential effects relative to the 68,000 Btu input by the heated air stream of the June 28 test.

1. Absorbed by the GAC

Roughly half the carbon was heated to a final temperature of 134 °F and half was at 94 °F when the test ended. Assuming a uniform initial temperature of 75 °F means that about 15,700 Btu were absorbed by the carbon. This represents 23% of the total net heat input.

Table D.3-1. Full-Scale Thermocouple Response Test (6/28/93)
Air Flow Analysis.

Air Flow			Cumulative Air Flow		
time (min)	cfm (75 °F)	lb/min	time (min)	lb/20 min	lb total
0	160	11.88	0	0	0
30	160	11.88	20	238	238
49	160	11.88	40	237	475
67	140	10.39	60	231	706
101	144	10.69	80	209	915
121	135	10.02	100	212	1,127
139	130	9.65	120	207	1,334
163	135	10.02	140	197	1,531
179	130	9.65	160	197	1,728
214	145	10.76	180	197	1,925
237	145	10.76	200	200	2,125
262	140	10.39	220	213	2,338
345	140	10.39	240	215	2,553
408	130	9.65	260	211	2,764
437	140	10.39	280	208	2,972
			300	208	3,180
			320	207	3,387
			340	208	3,595
			360	207	3,802
			380	202	4,004
			400	197	4,201
			420	195	4,396
			437	173	4,569

air density = 0.074 lb/ft³
air specific heat = 0.24 Btu/lb
°F

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GAC Canister Test (6-28-93)		Heat Input Analysis							
lb total	lb/30 min	Air Temperatures time (min)	time (min)	Tgas(in)	Tgas(out)		Heat Input to GAC System BTU/min	BTU (total) (30 min)	Cum. BTU
0	0	0	0	75	71		0	0	0
357	357	30	30	150	72		223	6,683	6,683
706	349	60	30	150	75		209	6,282	12,965
1021	315	90	30	150	77		184	5,519	18,484
1334	313	120	30	150	83		168	5,033	23,517
1630	296	150	30	150	86		152	4,547	28,063
1925	295	180	30	150	88		146	4,390	32,453
2232	307	210	30	150	89		150	4,494	36,948
2553	321	240	30	150	89		157	4,699	41,647
2868	315	270	30	150	89		154	4,612	46,259
3180	312	300	30	150	90		150	4,493	50,751
3491	311	330	30	150	90		149	4,478	55,230
3802	311	360	30	150	90		149	4,478	59,708
4103	301	390	30	150	90		144	4,334	64,043
4396	293	420	30	150	90		141	4,219	68,262
4712	316	450	30	80	90		-25	-758	67,503
5028	316	480	30	74	90		-40	-1,213	66,290
5344	316	510	30	73	87		-35	-1,062	65,228
5660	316	540	30	72	84		-30	-910	64,318
5976	316	570	30	71	82		-28	-834	63,484
6292	316	600	30	70	80		-25	-758	62,725
								62,725	(net - 10 hr)
								68,262	(net - 7 hr)

test628.xls

2. Heat of Desorption of Water Vapor from the GAC

The heat of desorption of residual water was calculated assuming a residual moisture content of 5% (from vendor data), one-half of the moisture desorbed during the test, and a heat of desorption equal to the latent heat of water. This heat sink accounts for 42,400 Btu, which is 62% of the total net heat input. Water desorption and GAC heat absorption account for approximately 85% of the heat input to the GAC system.

3. Absorbed by the Metal Canister

The canister weighs approximately 2,000 lb and has a heat capacity equal to that of steel (0.12 Btu/lb °F). An average wall temperature along the length of the canister was estimated from the wall temperature measurements as 80 °F and the initial wall temperature was estimated as 75 °F. The heat absorbed by the metal canister assuming a temperature rise of 80 to 75 °F is approximately 1,200 Btu. This amount accounts for 2% of the 68,000 Btu input by the air stream.

4. Losses from Airspace Above GAC

Because the system is not insulated, heat loss from the top region of the canister above the carbon bed is expected to be significant. An estimated temperature drop in the air stream of 10 °F from the canister inlet (150 °F) to the top of the carbon bed (140 °F), based on heat loss through the canister wall above the GAC, produces an additional calculated heat loss of 10,500 Btu, approximately 15% of the input heat.

5. Heat Loss Through the Canister Wall

The total canister surface area is about 100 ft². Using a reasonable surface-to-air heat transfer coefficient of 1 Btu/h ft² °F and a temperature driving force of 10 °F gives a total wall heat loss of approximately 7,000 Btu for a test run of 7 h. This is about 11% of the total heat input. The temperature driving force estimate is based on an average wall temperature of 85 °F taken along the length of the canister and an ambient temperature of 75 °F.

This estimate of wall heat loss is slightly larger than earlier wall loss estimates of 5% or less stated in the initial heat transfer modeling report. A 5% loss would amount to 3,200 Btu.

The table below is a summation of the above calculated heat losses for the GAC system.

1. Absorbed by the GAC	15,700	Btu
2. Used to desorb water vapor from the GAC	42,400	Btu
3. Absorbed by the metal canister	1,200	Btu
4. Losses from airspace above GAC	10,500	Btu
5. Lost through the wall of the canister	7,000	Btu
<hr/>		
Total calculated heat losses (1 through 5)	76,800	Btu
Total net heat input	68,000	Btu

The estimated heat sinks and losses exceed the total net heat input. This is not surprising when the number of assumptions required to make the calculations is considered. The agreement is remarkably good considering the number of assumptions.

By far the largest heat effect is that of the desorption of water from the carbon bed. This term alone accounts for roughly two-thirds of the total heat input. Second in importance is the heat absorption of the dried GAC, a minor factor relative to water desorption. Prior application of water to the GAC is a very effective heat sink term which may be used to advantage, if necessary, to suppress a potential GAC temperature rise.

The quantities of heat absorbed by the metal canister, lost from the airspace above the GAC, and lost through the canister wall are relatively small. All three calculations involved an estimation of a temperature difference based on limited data.

OVERALL HEAT TRANSFER COEFFICIENT

An attempt was made to calculate a GAC-to-air stream convective heat transfer coefficient, h ($\text{Btu/h ft}^2 \text{ } ^\circ\text{F}$), based on the net total heat input, a temperature driving force of 75 to 135 $^\circ\text{F}$, and an assumed carbon particle outside surface area of $250 \text{ ft}^2/\text{ft}^3$. The calculated value was much smaller than the originally estimated value of $9.9 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$. The test data are simply not the right type and are not precise enough to make such a calculation.

This does not mean that the use of the estimated value of $9.9 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$ is in error. To the contrary, the data and empirical correlations upon which the estimate was based were carefully derived from experiments designed specifically for that purpose. The current test data are not sufficient to make such a calculation.

NOTES ON FULL-SCALE THERMOCOUPLE RESPONSE TEST (6-28-93) DATA ANALYSIS

Figure D.3-1 shows the location of the thermocouples used to measure air, carbon, and wall temperatures during the test. The temperatures were automatically recorded every minute during the test. Air flow was measured intermittently.

INLET AND OUTLET AIR TEMPERATURES AND FLOWS

Figure D.3-2 shows the measured air temperatures as a function of time. Starting at the top of the figure the curves represent the heater exit (TC-12), the canister inlet (TC-10), and the canister outlet temperatures (TC-11), respectively.

TC-10 Inlet Air Temperature

Reasonably constant at 150 °F during test. Very sharp rise and sharp drop before and after test period, as expected. It appears that the inlet gas temperature was able to be controlled to about ± 1.5 °F during the test period, which ran for approximately 7 h and 20 min. Temperatures were in the range of 70 to 75 °F before and after the test.

TC-11 Outlet Air Temperature

Slow rise to a nearly constant temperature during test. Slow drop after test period. Starting at about 70 °F, about 2 h were required to achieve a temperature plateau of about 90 °F; after test period temperature held at plateau level for 1 h and then began to drop over a period of about 5 h to a low of about 72 °F at 13 h. After 13 h temperature reading became erratic.

The slow rise and slow fall are attributed to the fact that the GAC bed (and to a lesser extent, wall heat losses) removed heat from the inlet air stream at startup and added heat to the air stream on shutdown. The plateau temperature is indicative of steady-state heat removal by the GAC bed.

Inlet Air Flow

Intermittent air flow rate measurements were made over the test period. During the test, air flow was approximately 140 ft³/min. After the test period the air flow was maintained for another 14 h, the flow rate was not measured.

Analysis

Flows and temperatures were estimated at 30-min intervals and the net heat input was calculated based on the inlet and outlet gas temperatures. This net heat input was distributed as absorbed heat by the carbon, desorption/evaporation of water vapor from the carbon, transfer losses, wall losses, and heat absorbed by the canister. It is also possible that there is some heat of adsorption of water vapor onto the

Figure D.3-1. Location and ID of Thermocouples in Test Apparatus.

GAC Canister Thermocouple Operation

- Test performed with ambient temperature range of 73 to 76 degrees F.
- Test performed with ambient relative humidity range of 38% to 41%.
- Relative humidity at outlet 0526 into test was 44% at 90 degrees F.
- Airflow through canister ranged from 130 to 160 cfm and was typically 140 cfm.
- Test began 0931 6/28/93 and ended 0729 6/29/93.
- The airflow heater was shut off at 1550 6/28/93 (0619 into test).
- Airflow continued through the canister following heater shutdown.

Carbon and Canister

GAC Depth = 65 inches GAC Weight = 1750 pounds
 GAC Size Distribution - 4 x 10 mesh (1/16" x 3/16")
 Canister Diameter = 48 inches
 Canister Height = 7'10" Canister Weight = 2000 pounds

Thermocouple Locations

TC3, TC6, TC9 - located 16" below GAC surface
 TC4, TC7, TC10 - located 32" below GAC surface
 TC5, TC8, TC11 - located 48" below GAC surface
 TC2 - located 1" above GAC surface

Figure D.3-2. Air Temperatures Profiles as a Function of Time.

carbon as well as some low level of carbon gasification going on during the test period.

GAC BED TEMPERATURE MEASUREMENTS

Figure D.3-3 is a plot of the measured GAC bed temperatures as a function of time. As can be seen by the shape of the curves, a thermal wave passed the top two GAC bed thermocouples (TC-1 and TC-2). However, the test was stopped before it reached the bottom bed thermocouple (TC-3).

TC-1, TC-2, and TC-3 GAC Bed Temperatures

The GAC bed temperatures were measured by thermocouples TC-1, TC-2, and TC-3 placed 16, 42, and 48 in. from the top level of the bed, respectively. During the last 2 h of the test TC-3 was moved several times to help identify the location of the thermal wave as it progressed downward. TC-1 was also moved.

All three thermocouples showed an initial temperature rise to a steady temperature of about 90 to 95 °F. This is an equilibrium temperature caused by the heat sink effect of water vapor desorbing/evaporating from the carbon. After the water vapor was completely removed, TC-1 and TC-2 rose to a final steady (in the case of TC-1) temperature of about 132 to 134 °F. This higher temperature occurred when the dried GAC itself absorbed heat from the air stream.

Analysis

A heat absorption thermal wave was definitely noted as evidenced by the shapes of the temperature profile curves. After an initial temperature plateau "waiting period" during which residual moisture retained by the GAC was desorbed/evaporated, there was a sharp rise in temperature by the TC-1 and TC-2 thermocouples indicative of a heat absorption wave moving downward through the bed. This wave arrived at the thermocouples at approximately 3 and 7 h, respectively. The test was not run long enough for the thermal wave to reach TC-3.

Towards the end of the test, TC-3 was moved upward between TC-1 and TC-2 to identify the location of the thermal wave generated between the plateau heat sink effect of the desorbing water vapor and the final, dry carbon equilibrium temperature. Temperatures between 95 and 134 °F were measured a few inches above TC-2 between 5½ and 6½ h, just prior to its final rise to 134 °F.

In the presence of mass transfer/adsorption with its attendant heat of adsorption effect it should be possible to detect a similar thermal wave in the GAC and, thus, identify the position of the mass transfer zone as it progresses through the column.

It should be noted that the measured temperatures are the result of a physical averaging of actual gas and GAC temperatures and are not a single component.

GAC Canister Test

Idealized Plot

Figure D.3-3. GAC Bed Temperature Profiles as a Function of Time.

CANISTER TEMPERATURE MEASUREMENTS

TC-4, 5, 6 and TC-7, 8, 9 Canister Wall Temperatures

Thermocouples TC-4, TC-5, and TC-6 measured the outside canister wall temperatures at levels identical to the GAC bed thermocouples (i.e., 16, 32, and 48 in. below the bed surface) and at a position 180° from the gas inlet and outlet ports (i.e., opposite side from the ports). Likewise, thermocouples TC-7, TC-8, and TC-9 measured the outside canister wall temperatures at identical levels at a position inline with the gas inlet and outlet ports.

The temperature profiles for the bottom four thermocouples (TC-5, TC-6, TC-8, and TC-9) are virtually identical over the test period. All started at 72 or 73 °F and rose to 78 ° to 80 °F after about 3 to 4 h. All held steady at this temperature for the duration of the test. After air heating stopped all temperatures declined slowly over many hours.

The temperature profiles for the top two thermocouples (TC-4 and TC-7) are similar with two exceptions. Both rose to a slightly higher temperature of 84 to 87 °F and thermocouple TC-4 (opposite the ports) was slightly higher. Otherwise, the profiles were similar.

Analysis

The low wall temperatures indicate low wall heat loss. Relatively speaking, the inlet air was at 150 °F and the maximum carbon temperature was 134 °F, whereas the typical wall temperature was 80 to 85 °F.

The slightly higher maximum temperature for the two top wall thermocouples (TC-4 and TC-7) is attributable to the slow redistribution of absorbed heat by conduction from the warm GAC to the wall. Slow conductive heat transfer between the GAC and the wall may be possible since there was an appreciable temperature driving force (134 to 80 °F) in that region for a period of several hours.

ATTACHMENT D.4

ANALYSIS OF SECOND FULL-SCALE THERMOCOUPLE RESPONSE TEST
JULY 20 TO JULY 23, 1993

ATTACHMENT D.4
ANALYSIS OF SECOND FULL-SCALE THERMOCOUPLE RESPONSE TEST
JULY 20 TO JULY 23, 1993

The test reported here is identical to the earlier June 28 (Attachment D.3) test except that it was run for approximately 64 h. This increased run time, which included an initial 14.8-h unheated air equilibration period, a 16.2-h heated air test run, and a 33.5-h unheated air cool-down period, allowed the thermal wave front to move completely through the GAC bed. Additional temperature and relative humidity measurements were also incorporated in this test.

The notes at the end of this report present plots and discuss the temperature, air flow, and relative humidity time profiles for the entire test. The discussion here presents the results of heat balance and moisture calculations for the full-scale GAC bed and air flow systems test setup.

HEAT INPUT CALCULATIONS

Electrically heated inlet air was the sole heat source for this test. There were no measured heat of adsorption effects due to adsorption of water vapor during the unheated pretest airflow period or the cool-down period. Air flow and temperature versus time are presented in the notes to this report. Knowing the air flow rate and temperature at various points allowed estimation of heat input and heat losses to the GAC system. The additional thermocouple 1-in. above the GAC bed allowed more accurate interpretation of the temperature data.

The following table lists the heat inputs and heat losses calculated from the test data during the heated portion of the test run. The total net heat input and heat losses were calculated based on measured air flow and temperature at various points in the GAC system.

Total net heat input to the GAC system	250,700	Btu
a. Heat loss from heater to canister inlet port	107,200	Btu
b. Heat loss from inlet port to top of GAC	29,900	Btu
c. Net heat input to the GAC	113,600	Btu

Over half the total net heat input was lost before reaching the GAC. This results from the flexible hose air flow line and the top of the canister being uninsulated as well as the high air temperature which provides a greater driving force for heat loss. These totals are for the 16.2-h test run, assuming thermal equilibrium prior to starting the test.

HEAT DISTRIBUTION WITHIN THE GAC SYSTEM

The GAC system includes the carbon bed, the moisture in the carbon bed and the metal canister. The net heat (113,600 Btu) reaching the GAC system is distributed among these items.

Two of the largest heat sinks in the system are expected to be the moisture contained in the carbon and the carbon bed itself. As the heated air moves through the bed, water is desorbed (evaporated) from the carbon. After the water is removed, the carbon itself will absorb heat from the air. These two phenomena account for the temperature plateau and the thermal wave noted in the analysis of the GAC thermocouples.

Assuming (1) the vendor's value of 5% moisture in the carbon, (2) all the moisture is desorbed, and (3) the heat of desorption is equal to the latent heat of water, the moisture heat sink effect is estimated to consume 84,900 Btu.

Likewise, assuming a specific heat of GAC of 0.20 Btu/lb °F, the heat sink effect of the GAC is estimated as 21,000 Btu. These results are summarized in the listing below.

Net heat input to the GAC system	113,600	Btu
<hr/>		
a. Moisture heat sink	84,900	Btu
b. GAC heat absorption	21,000	Btu
c. Net heat lost or absorbed	7,700	Btu

It should be noted that the moisture heat sink is four times greater than the heat sink of the GAC alone. This is dramatic evidence of the effectiveness of moisture as a means of heat removal from carbon beds and illustrates the practice of prewetting as a technique for minimizing bed heating.

The net heat lost or absorbed (7,700 Btu) is distributed between heat absorbed by the metal canister and heat lost through the wall of the canister. If it is assumed that the steel canister, which has an approximate weight of 2,000 lb and specific heat of 0.12 Btu/lb °F, experiences an average temperature rise of 5 °F, then the absorbed heat totals 1,200 Btu.

The remaining 6,500 Btu are assumed to be lost through the canister wall. This heat amounts to roughly 3% of the total input heat; a figure in agreement with earlier wall heat loss estimates of less than 5%. Calculation of a wall-to-ambient convective heat transfer coefficient for the canister produces a value of $h_w = 0.5 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$. This value is slightly lower, but quite reasonable in comparison with published wall coefficient values. A review of adsorption modeling literature revealed estimates and calculations of this coefficient for various situations to be in the range of $h_w = 1$ to $28 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$.

It was not possible, with the test data given, to estimate a GAC-to-air stream convective heat transfer coefficient h_g . An estimate of h_g using empirical methods from the literature resulted in a value of $h_g = 9.9 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$. A review of adsorption modeling literature produced an estimate of $h_g = 72 \text{ Btu/h ft}^2 \text{ } ^\circ\text{F}$.

RATE OF THERMAL WAVE TRAVEL

An estimate of the rate of travel of the thermal wave through the GAC-filled canister may be made by noting the times at which the bed thermocouples rise from their plateau to their final temperatures. This estimate is tabulated below.

Δ length (in.)	Δ time (h)	rate (in./h)
16	4.1	3.90
32	8.1	3.95
48	11.5	4.17

		avg = 4.00 in./h

At this rate, it would require 16.2 h for the thermal wave to pass through the canister, which is precisely the amount of time that the heater operated.

Several factors affect the rate of travel of the thermal wave. The most important factors are the air flow rate and temperature, the air flow contaminant (solvent) concentration, carbon moisture, and carbon bed cross-sectional area.

HUMIDITY/MOISTURE MASS BALANCE CHECK

Throughout this analysis a GAC moisture content of 5% has been used, based on vendor information. One check of the validity of this number was made in the heat distribution calculations. In that case, the heat sink of 5% moisture accounted for 75% of the net heat input. The 5% moisture value is, thus, a reasonable one.

However, a more conclusive estimate of GAC moisture can be made by calculating the difference between inlet and outlet humidities. By calculating this humidity difference and relating to air flow and time a mass balance check on GAC moisture may be made.

As seen in Figure D.4-7, ambient relative humidity varied with temperature and in a daily cycle. However, absolute humidity varied by only about 10% during the daily cycle. A value of 0.0075 lb water/lb dry air was calculated as the average inlet absolute humidity. Likewise, canister outlet air relative humidity, as seen in Figure D.4-7, changed little during the test period. An average outlet absolute humidity for the test was 0.160 lb water/lb dry air.

This humidity difference across the canister when combined with the air flow rate produced an estimate of 84 lb of net water loss from the GAC during the test. This amount of water corresponds to a 4.8% moisture content on the GAC; certainly, within experimental error. Thus, the assumption and use of 5% GAC moisture is valid.

Apparently, the prior use of this canister for a similar test on June 28 had no impact on moisture content for this test. In the earlier test approximately half of the GAC was dried judging from the position of the thermal wave when the test was stopped. It is likely that the 14.8-h unheated air flow at the beginning of the current test equilibrated the bed moisture content to an approximate 5% level.

NOTES ON FULL-SCALE THERMOCOUPLE RESPONSE TEST OF 7-20-93 DATA/ANALYSIS

The test of July 20, 1993 ran for a period of approximately 64 h. This longer test was performed in order to allow all three bed thermocouples to achieve thermal equilibrium during the heating period. In addition, long startup and shutdown, unheated air flow periods were incorporated to achieve steady-state conditions prior to and after heating.

Additional instrumentation was used in this test. Ambient temperature, ambient relative humidity, canister exit relative humidity, and the air temperature 1 in. above the carbon bed were new data points measured in addition to the data points taken during the June 28 test. Temperatures and relative humidities were measured automatically every 5 min. Air flow was measured intermittently.

Figure D.4-1 is the key to the measurement devices and their locations in the test apparatus.

AIR FLOW

Air flow was maintained approximately constant throughout the 64-h test. The first 14.8 h and the last 33.5 h of the test the air flow was unheated. For 16.2 h the air was heated by an electrical device before it entered the canister. The heated air flow desorbed water from the carbon bed and caused a thermal wave front to advance from top to bottom of the bed.

Air flow was measured in the canister exit line at irregular intervals. Air flow rates measured during the test are shown in Figure D.4-2. Air flow averaged 136.5 stdft³/min for the test.

AIR STREAM TEMPERATURES

Four thermocouples measured air stream temperatures during the test. Plots of these temperatures are shown in Figure D.4-3.

TC-14 Heater Exit Temperature

While the heater was operating the exit gas temperature was approximately constant at slightly less than 200 °F. The air temperature response to the heater being turned on or off was instantaneous.

TC-12 Canister Inlet Temperature

The air stream temperature measured at the canister inlet was constant at 150 °F during the test. The 10-ft-long, flexible hose connection from the heater to the canister was uninsulated. This allowed a 50 °F temperature drop in the line. Temperature response was instantaneous.

Figure D.4-1. Measurement Device IDs and Locations.

GAC Canister Thermocouple Operational Test

- Test began at 1536 7/20/93 and ended 0745 7/23/93 (lasted approx. 65 hours).
- The air flow heater was operated from 0600 to 2210 on 7/21/93 (16 hrs 10 min).
- Temperature and humidity recorded every 5 minutes at locations shown below.
- Air flow measured intermittantly throughout test averaged about 136 SCFM.
- Ambient relative humidity (RH) ranged from 29% to 61% during test.
- Ambient temperature ranged from 64° to 77° during test.

Carbon and Canister

GAC Depth = 65 inches GAC Weight = 1750 pounds
 GAC Size Distribution - 4 x 10 mesh (1/16" x 3/16")
 Canister Diameter = 48 inches
 Canister Height = 7'10" Canister Weight = 2000 pounds

Thermocouple Locations

TC3, TC6, TC9 - located 16" below GAC surface
 TC4, TC7, TC10 - located 32" below GAC surface
 TC5, TC8, TC11 - located 48" below GAC surface
 TC2 - located 1" above GAC surface

Figure D.4-1. Measurement Device IDs and Locations.

Figure D.4-2. Air Flow Versus Time for Test of July 20 to 23, 1993.

Figure D.4-3. Air Stream Temperatures Versus Time.

TC-2 Carbon Bed Inlet Temperature

A thermocouple mounted 1 in. above the center of the carbon bed measured the air temperature just before entering the bed. This was a new thermocouple location added since the June 28 test. The bed inlet temperature was constant and averaged 138 °F for the test.

TC-13 Canister Outlet Temperature

It was noted in the test notes that TC-13 appeared to have been in contact with the canister outlet valve. Thus, its measurements are in doubt. There appears to be a sluggish rise to about 90 °F in response to the heated air input. This temperature was constant for the test period. After the heated air was turned off the temperature unexpectedly rose to 104 °F before slowly tapering off over the final 30 h of the test. Perhaps, if this thermocouple was contacting the metal valve, the temperature rise may have been due to heat conduction through the metal.

GAC BED TEMPERATURES

Three thermocouples, TC-3, TC-4, and TC-5, measured the GAC bed temperature during the test. These three thermocouples were located near the centerline of the canister at depths of 16, 32, and 48 in. (representing 25%, 50%, and 75% of the total bed depth). Figure D.4-4 shows the GAC bed temperatures during the test.

All three temperature profiles have a similar shape. Each curve rises from a starting temperature of about 75 °F to a plateau temperature of 97 °F and then rises to a final temperature of 137 °F. The only differences among the curves is the length of time at the plateau temperature and at the final temperature. The temperature responses to the heater being turned on and off are not instantaneous, but lag by only a few min.

The plateau temperature is the equilibrium temperature attained while water is being desorbed from the GAC. The desorption of water is a heat sink that must be completely removed before the temperature rises higher. The final GAC temperature is an equilibrium among the dried heated carbon, the incoming heated air, and canister heat absorption and losses.

A heat absorption wave front was noted passing each of the three thermocouples at 4.1, 8.1, and 11.5 h, respectively. This corresponds to an average wave velocity of about 4.0 in./h. At this rate the heat absorption wave would require 16.2 h to completely desorb water and warm the bed.

Bed cooling, even with air flow, is quite slow as seen in Figure D.4-4. As discussed below, very long times were needed to cool the GAC. This experience is in agreement with literature reports, field experience, and with the Biot number calculation reported elsewhere. The Biot number calculation revealed that heat dissipation from the GAC system is limited by the slow conduction of heat from the carbon particles.

Figure D.4-4. Carbon Bed Temperatures Versus Time.

TC-3 GAC 16-in. Temperature

The top bed thermocouple was at an average plateau temperature of 95 °F for 4.1 h before rising to a 135 °F final temperature for 12.5 h. After the heater was turned off 1.8 h was required for the temperature to drop below 100 °F and 6.0 h to drop below 85 °F.

TC-4 GAC 32-in. Temperature

The middle bed thermocouple was at an average plateau temperature of 98 °F for 8.1 h before rising to a 135 °F final temperature for 8.7 h. After the heater was turned off 3.7 h was required for the temperature to drop below 100 °F and 13.9 h to drop below 85 °F.

TC-5 GAC 48-in. Temperature

The bottom bed thermocouple was at an average plateau temperature of 97 °F for 11.5 h before rising to a 135 °F final temperature for 5.6 h. After the heater was turned off 6.3 h was required for the temperature to drop below 100 °F and 20.3 h to drop below 85 °F.

CANISTER WALL TEMPERATURE

The canister wall temperature was measured at 16-, 32-, and 48-in. levels (from the top of the GAC) at vertical locations inline with the air inlet/outlet ports (0° location, TC-9, TC-10, and TC-11) and opposite the inlet/outlet ports (180° location, TC-6, TC-7, and TC-8). Figures D.4-5 and D.4-6 show the measured temperatures. The curves for the two locations are remarkably similar, indicating radial temperature symmetry in the canister.

After a slow decline due to cooling by the startup air flow, wall temperatures quickly rose 5 to 10 °F in response to the heater and, thereafter, slowly rose for the duration of the test with peak temperatures never exceeding 90 °F. The slow rise occurred due to the gradual dissipation of the water heat sink, the eventual conduction of heat by the GAC to the wall, and the high thermal conductivity of the metal wall relative to the GAC.

TC-6 and TC-9 Wall 16-in. Temperature

The maximum wall temperatures of just under 90 °F were reached by the top two thermocouples. This occurred because the top of the bed experienced the thermal wave first, making more time available for the slow conduction of heat from the GAC to the wall. The other thermocouples did not have as much time to reach similar temperatures.

TC-7 and TC-10 Wall 32-in. and TC-8 and TC-11 Wall 48-in. Thermocouples

The temperature curves of the lower thermocouples were nearly identical. The middle thermocouple was 1 to 2 °F higher than the lower thermocouple.

Figure D.4-5. Canister Wall (0) Temperatures Versus Time.

Figure D.4-6. Canister Wall (180) Temperatures Versus Time.

D.4-15

AMBIENT CONDITIONS

There was a diurnal cycle to both ambient temperature and relative humidity as shown in Figure D.4-7. The daily temperature in the laboratory varied by approximately 10 °F. The ambient relative humidity varied from 29% to 61%. Ambient temperature maxima corresponded to relative humidity minima.

TC-1 Ambient Temperature

Peak ambient temperatures measured during the test were 76, 77, and 76 °F, and minimum temperatures were 64 and 67 °F.

RH-2 Ambient Relative Humidity

Peak ambient relative humidities measured during the test were 57% and 61%, and minimum relative humidities were 36%, 29%, and 42%.

CANISTER EXIT RELATIVE HUMIDITY

The canister exit relative humidity RH-1, shown in Figure D.4-7, peaked at 62% when the heater was turned on. During this time warm air desorbed water from the GAC. The RH declined very slowly during the test run as water was desorbed from the GAC. When the heater was turned off the canister exit relative humidity dropped slowly to a minimum of 15%. During the unheated air flow following the test, the dried GAC began to adsorb water vapor.

Figure D.4-7. Ambient Temperature and Relative Humidity Versus Time.

ATTACHMENT D.5

BENCH-SCALE ADSORBER TESTS
PHASE I TESTING
AUGUST 4 TO AUGUST 18, 1993

PHASE I LABORATORY BENCH-SCALE TESTING OF GAC ADSORPTION

SUMMARY

From August 4 to August 18, 1993, laboratory bench-scale tests were performed on GAC adsorption of carbon tetrachloride at the Department of Civil and Environmental Engineering at WSU. The purpose of this testing was to determine the effects of GAC adsorption on a scale that could be directly related to field production. Testing was also performed on interior and exterior canister paint coupons to determine operating temperature limits.

A 3-in.-diameter by 6-ft-long GAC-filled test column was constructed from ordinary pipe and instrumented such that temperatures, flows, and relative humidities were automatically recorded. The inlet concentration of carbon tetrachloride was controlled over a nominal range from 1,000 to 30,000 ppm_v. Tests were also performed with 200 ppm_v levels of MEK introduced with the carbon tetrachloride. Flow rates were scaled to duplicate actual field design flows.

A repeatable and predictable thermal wave was observed to move through the GAC. As the inlet carbon tetrachloride concentration increased, the thermal wave peaks became much larger and sharper in profile. The GAC temperature increases of over 190 °F were measured for inlet 30,000 ppm_v carbon tetrachloride concentration. Low inlet concentrations of carbon tetrachloride produced low peak temperatures and broad wave profiles. At inlet 1,000 ppm_v carbon tetrachloride concentration the temperature rise was 5 °F.

There was no measured effect of including 200 ppm_v MEK in the inlet concentration for the 1,000 ppm_v carbon tetrachloride run. When the MEK was added to 5,000 ppm_v carbon tetrachloride, a temperature increase of 5 °F was noted.

Fresh and loaded GAC samples at room temperature were mixed with deionized water that was then tested for pH. All samples had a measured pH of less than 9.3.

TEST EQUIPMENT SETUP

The test equipment setup for this adsorption study is shown in Figure D.5-1. The setup consisted of an inlet stream preparation area, the GAC column, a discharge adsorber, and a laboratory fume hood. Shown are the locations of instruments for measuring temperature, flow, and relative humidity. Data were collected every minute by automatic data loggers.

1. Inlet Stream Preparation

A small laboratory blower was used to feed the column. Flow was modulated by a rheostat that controlled the speed of the blower. Ambient air was used. Ambient air temperature and relative humidity were measured automatically and the feed flow rate recorded manually. The feed stream was dosed

Figure D.5-1. Bench-Scale Phase I Test Equipment Schematic.

in a controlled manner with carbon tetrachloride or carbon tetrachloride plus MEK as shown in Figure D.5-1.

The dosing apparatus was set up in a laboratory hood. It consisted of a small laboratory blower controlled by a rheostat, appropriate valves and rotameters, and a flask containing liquid carbon tetrachloride. The flask was set in a temperature-regulated bath to control volatility and thereby the concentration of carbon tetrachloride. The air flow rate through the flask was also used to control concentration. The carbon tetrachloride stream was introduced to the bulk feed stream ahead of the flowmeter. The combined stream was fed to the canister by a flexible hose connection. An identical, parallel system was used to add MEK to the feed stream.

Just prior to the test column, the feed concentration of carbon tetrachloride was measured by collecting a sample in a gas collection bag and performing offline measurement using an analytical meter. For the case of a carbon tetrachloride plus MEK feed, a sample was collected and analyzed by a gas chromatograph to determine the exact inlet concentration.

2. Test Column

The test column consisted of a 6-ft-long, 3-in.-diameter steel pipe. A 3-in. tee was attached at both ends with one leg blanked so that the flow stream made right angle turns entering and exiting the column. Gas stream sample ports were located in both tees. Temperature and relative humidity were automatically measured at the exit tee. The column was surrounded with a molded sleeve of 1-in.-thick fiberglass insulation.

Literature reports and a telephone conversation with a national GAC expert and published experimentalist, confirmed the design of the GAC column. With adequate insulation to minimize wall heat loss, such a configuration is directly scaleable to the field canister.

The test column held 9.0 lb of virgin GAC. Virgin GAC was loaded for each test run.

The column was instrumented with 18 thermocouples. Thermocouples were inserted through the column wall perpendicular to the flow stream on the centerline of the pipe. Thermocouple locations were as follows:

<u>Thermocouple</u>	<u>Location</u>
TC-6	Entrance tee, above GAC
TC-7	3½ in. below GAC surface*
TC-8	7 in. below GAC surface
TC-9	10½ in. below GAC surface*
TC-10	14 in. below GAC surface
TC-11	17½ in. below GAC surface*
TC-12	21 in. below GAC surface
TC-13	24½ in. below GAC surface*
TC-14	28 in. below GAC surface
TC-15	31½ in. below GAC surface*
TC-16	35 in. below GAC surface
TC-17	42 in. below GAC surface
TC-18	49 in. below GAC surface
TC-19	56 in. below GAC surface
TC-20	63 in. below GAC surface
TC-21	70 in. below GAC surface
TC-22	Exit tee, below GAC
TC-23	On outer surface of pipe, 43 in. below GAC surface

*These thermocouples were installed following Test Run 1 and prior to Test Run 2.

3. Discharge Adsorber

The exit stream from the test column was connected by a flexible hose to a discharge adsorber located in the exhaust hood. The discharge adsorber was loaded with an excess of GAC to adsorb any carbon tetrachloride or carbon tetrachloride/MEK mixture emitted from the column. The exhaust from the discharge adsorber was emitted to the hood.

TEST PLAN

A total of seven test runs were made. Inlet carbon tetrachloride concentration was the principal variable studied. However, for two runs a mixture of carbon tetrachloride and MEK were fed to the canister. In addition, near the end of Tests 1 and 5 the flow was reduced by half to determine its effect on GAC temperature rise. Ambient air conditions were uncontrolled, but were steady for all tests at approximately 60% RH at 72 °F.

The following table lists the experimental conditions for each test run.

Test Plan

Test	Inlet CCl ₄ (ppm _v)	Inlet MEK (ppm _v)	Superficial velocity (ft/m)
1	1,000	0	40
2	1,000	200	40
3	5,000	0	40
4	5,000	200	40
5	10,000	0	40
6	20,000	0	40
7	30,000	0	40

NOTE: Tests 1 and 5 superficial velocities reduced to 20 ft/m near end of test.

The test superficial velocity of 40 ft/m corresponds to a field canister design flow of 500 ft³/min. This flow was manually controlled and held constant during the tests. In fact, all variables were manually controlled and held steady for each test. For example, inlet carbon tetrachloride concentration was measured offline, but typically varied by less than +/- 5%. This variable was controlled by regulating flow and maintaining a constant temperature of the liquid carbon tetrachloride.

At the conclusion of each test the column contents were allowed to cool either by stopping all flow and allowing the heat to dissipate slowly or by maintaining ambient air flow with no concentration of carbon tetrachloride or MEK. The cooled GAC was removed from the column. The GAC that had reached a temperature maximum and, hence, was fully loaded was separated and a portion was tested for pH by an industry-accepted standard method.

TEST RESULTS

The most obvious and dramatic results of the GAC adsorption testing were as follows:

- The consistency of the thermal wave temperature peak and profile as the wave progressed down the column
- The linear relationship of peak temperature with inlet carbon tetrachloride concentration.

Figure D.5-2 is a plot of maximum observed temperatures versus inlet carbon tetrachloride concentration. At inlet concentration of 1,000 ppm, the measured peak temperature rise was only 5 °F above ambient temperature. This is typical of operation at the 216-Z-1A Tile Field at which measured inlet

Figure D.5-2. Observed Bench-Scale Test GAC Peak Temperatures.

concentrations never exceeded 1,000 ppm, and no thermal effects were ever noted, nor actually measured.

However, during the June 3 incident at the 216-Z-9 Trench the measured inlet concentration of 28,500 ppm, should have produced a temperature rise of about 180 °F according to Figure D.5-2. Such a rise corresponds to a GAC temperature of approximately 260 °F. While this temperature was not sufficient to discolor the canister paint, it may have been high enough to promote other exothermic reactions that may have added to the temperature rise.

Figures D.5-4 through D.5-10 in Attachment D.5-1 are plots of temperature versus time for each of the seven test runs. A discussion of the details of the plots is given in Attachment D.5-1; however, a few important features are mentioned here.

Generally speaking, the greater the inlet concentration, the larger the temperature rise and the sharper and narrower the peak profile. High inlet concentrations had large, sharp, narrow peaks. Low inlet concentrations had small, flat, broad peaks. Also, as a test run progressed and the wave moved down the column, the peak profiles tended to broaden slightly at the base.

Effects of MEK

There was no apparent impact on GAC temperature rise with an additional 200 ppm, MEK in the inlet stream at carbon tetrachloride levels of 1,000 ppm. At 5,000 ppm, a temperature rise of approximately 5 °F occurred due to the MEK. A comparison of Figures D.5-4 and D.5-5 shows an approximate 3 °F temperature rise for both the 1,000 ppm, carbon tetrachloride inlet concentration and the 1,000 ppm, carbon tetrachloride with 200 ppm, MEK inlet concentration tests. At an inlet concentration of 5,000 ppm, carbon tetrachloride, Figures D.5-6 and D.5-7 show an increase of 5 °F with the additional 200 ppm, MEK. In his paper "Spontaneous Combustion of Carbon Beds," A. A. Naujokas concludes, for a slightly different test procedure, that cosolvents tend to lessen the oxidative activity of the system (Appendix B). Hence, the lack of a significant effect at these low concentrations and short test times is not surprising.

If there were a very slow temperature rise attributable to MEK either through heat of adsorption or heat of reaction/combustion, it may be the case that these test runs were too short duration to see a significant effect. Additionally, increased concentrations of MEK and/or carbon tetrachloride may possibly produce an additional temperature rise effect. Further testing for longer periods of time and at higher concentrations would be required to prove or disprove this possibility.

Data Analysis

Listed below are technical specifics relating to the bench-scale adsorber tests.

GAC in Adsorber:	9.04 lb
Superficial Air Velocity:	40 ft/m (equivalent to production 500 ft ³ /min) 2.05 ft ³ /m 0.152 lb air m

Inlet CCl_4 Concentration (ppm)	CCl_4 Loading Rate (lb/h)	Thermal Wave Rate (in./h)	Calc. GAC Loading (lb CCl_4 / lb GAC)
1,000	0.049	1.4	0.29
5,000	0.246	6.9	0.36
10,000	0.491	8.9	0.42
20,000	0.982	18.2	0.47
30,000	1.474	22.5	0.50

The carbon tetrachloride loading rate is calculated from the inlet carbon tetrachloride concentration and air flow rate. The rate of travel of the thermal wave was calculated by measuring the timing of the wave peaks of the ΔT versus time plots for each test run (see Attachment D.5-1, Figures D.5-1 through D.5-10). This thermal wave rate is also comparable to the production canister operating at design flow and corresponding inlet concentration.

The GAC loading values, as well as all other analytical calculations in this test report, were calculated from data applicable over the first 14 in. of GAC bed and assuming total carbon tetrachloride adsorption (i.e., no breakthrough, a good assumption over the first 14 in. of the GAC). The GAC loading values should also be applicable to production-scale operations at corresponding inlet concentrations. This increasing trend of GAC loading with increasing inlet carbon tetrachloride concentration agrees with adsorption theory. Figure D.5-3 shows plots of GAC loading and thermal wave rate as functions of inlet concentration.

Scale-Up Effects

One published researcher who has done experimental work in the investigation of carbon bed fires was contacted prior to testing for advice on test equipment sizing and test procedures. He suggested a test column length identical to the production situation for confidence in extrapolation of test results to production scale.

Much of his past experimental work was done in well-insulated or heated 2-in.-diameter columns. The insulation or heating was provided to minimize wall heat loss and make the test apparatus behave similarly to larger diameter production operations. He felt that a 3-in. insulated pipe would be adequate for this test.

Figure D.5-3. GAC Loading and Thermal Wave Rate Versus Inlet CCl_4 Concentration.

One effect that was not compensated for was the thermal mass effect of the pipe wall relative to the GAC. For the test apparatus, the product [(mass) x (heat capacity)] for the pipe was 5.5 Btu/°F and for the GAC was 2.2 Btu/°F, which means that the pipe is capable of absorbing 2.5 times as much heat as the GAC, given the same temperature driving force. This same ratio calculated for the production case of a 2,000-lb canister and 1,760 lb of GAC gives a ratio of 0.6. Hence, there is roughly a factor of 4 (i.e., = 2.5/0.6) difference from the test to the production cases.

This is a small factor; nevertheless, it means that the test apparatus may underestimate the adsorption temperature rise. This is probably not a factor for small ΔT , but becomes more important as ΔT increases.

Wall flow effects can potentially become a factor in scale-up. Wall flow would bypass GAC and produce larger than expected outlet carbon tetrachloride concentrations. An accepted rule of thumb is that wall flow is negligible if the pipe diameter is a minimum of 10 times the diameter of an average particle, which is the case for this test. However, data analysis reveals that outlet carbon tetrachloride concentrations were detectable, but very small. Thus, there were no appreciable wall flow effects.

Heat Rate/Temperature Analysis

The heat rate and temperature rise data in the following table are based on calculations over the first 14 in. of GAC. This basis was chosen because data for the five inlet concentrations could be compared.

The time required for the thermal wave to reach the 14-in. thermocouple was derived from the experimental data in Figures D.5-4 through D.5-10. The total air flow was calculated from the known flow and the time value from column two of the table. Total Btu input from the heat of adsorption was calculated from the heat of adsorption and carbon tetrachloride adsorbed for each inlet concentration. The values in this column are somewhat scattered because the calculation was based on the experimental results. The calculated temperature rise was derived by dividing the total Btu input by the product of the total air flow and the specific heat of air (assumed constant at 0.24 Btu/°F lb).

Inlet Conc. (ppm, CC1 ₄)	Time of Wave to 14 in. (h)	Total Air Flow (lb)	Total Btu Input	Calc. Temp Rise (°F)	Max. Temp Rise (°F)
1,000	10.00	91.2	70	3	5
5,000	2.60	23.7	109	19	27
10,000	1.50	13.7	89	27	54
20,000	0.86	7.8	116	62	137
30,000	0.60	5.5	100	76	193

The calculated temperature rise is much less than the actual, measured temperature rise. There are several possible reasons for this. First, multiple calculations were required using the experimental data and, undoubtedly, there is appreciable experimental error in the values. This error could only be reduced by replicate testing. An implicit assumption in doing this calculation was that the GAC and air temperatures are identical and follow each other instantaneously. This is not true because the insulating nature of GAC will produce a temperature profile across a GAC particle. Hence, it is impossible for the GAC and the air stream temperatures to be equal, except momentarily.

ATTACHMENT D.5-1

This attachment discussion covers the plots of Figures D.5-4 through D.5-10. These plots of temperature and flow versus time for each of the seven test runs are not comprehensive compilations of all the test data, but do represent the most meaningful portions.

Tests are identified by the numbers 1 through 7 given at the top center of each plot. The key test variable, which was the inlet stream concentration, is given just below the test number. See the main body of text for the Test Plan.

For all tests (except as noted for Tests 1 and 5) the inlet superficial velocity was maintained at 40 ft/m. This superficial velocity is the same as a 500 ft³/min design flow for the production GAC canisters.

For each test, temperature data for the first four thermocouples to experience the thermal wave are plotted. These thermocouples were located at positions 3.5, 7.0, 10.5, and 14.0 in. from the surface of the GAC (except for Test 1 for which the locations were 7.0, 14.0, 21.0, and 28.0 in.). Figures D.5-4, D.5-6, D.5-7, D.5-8, and D.5-9 show temperature values are not actual temperatures; Figures D.5-5 and D.5-10 show temperature rise experienced by each thermocouple.

The duration of the test runs are variable as can be seen on the x-axis. For the low inlet concentration runs the test were very long because the GAC loading rate was low; high inlet concentration test runs were shorter because the GAC loading rate was higher.

The larger the inlet concentration the larger the temperature rise and the sharper and narrower the peak profile. High inlet concentrations had large, sharp, narrow peaks. Low inlet concentrations had small, flat, broad peaks. Also, as a test run progressed and the wave passed through the column, the peak profiles tended to broaden slightly.

TEST 1 AND TEST 2

Test 1 was run at an inlet carbon tetrachloride concentration of 1,000 ppm, and a superficial velocity of 40 ft/m (500 ft³/min production). Total test time was 42 h. For the last 18 h the superficial velocity was reduced to 20 ft/m (250 ft³/min production). Temperatures were measured at 7, 14, 21, and 28 in. from the GAC surface.

Test 2 was run at an inlet concentration of 1,000 ppm, of carbon tetrachloride and 200 ppm, of MEK. Superficial velocity was constant at 40 ft/m (500 ft³/min production). Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the surface of the GAC. Total test time was 18 h.

As can be seen on the temperature scale, temperature rises for both tests were very small. In fact, it appears that the temperature rise may be partly attributed to a difference in temperature between the GAC and the flow stream. Undoubtedly, mass adsorption and convective cooling are going on in the GAC as confirmed by inlet and outlet carbon tetrachloride measurements.

However, all downstream thermocouples rose in temperature more or less together and much sooner than a thermal wave caused by heat of adsorption. This seems to be confirmed for Test 1; when the superficial velocity is decreased to 20 ft/m there is a corresponding decrease in temperature.

There was an 0.5 °F temperature rise difference due to the additional presence of 200 ppm, MEK for the test runs.

TEST 3 AND TEST 4

Test 3 was run at an inlet carbon tetrachloride concentration of 5,000 ppm, and a superficial velocity of 40 ft/m (500 ft³/min production). Total test time was 3.8 h. Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the GAC surface.

The peak temperature rises and associated times for the first four thermocouples were 22.0 °F at 25 min, 28 °F at 52 min, 22 °F at 112 min, and 23 °F at 156 min. This computes to an average peak temperature rise of 24 °F and thermal wave rate of travel of 6.9 in./h. The test was stopped because of the consistency of the wave peaks and the time pressure to test at other conditions.

Test 4 was run at an inlet concentration of 5,000 ppm, of carbon tetrachloride and 200 ppm, of MEK. Superficial velocity was constant at 40 ft/m (500 ft³/min production). Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the surface of the GAC. Total test time was 3.5 h.

Test 4 temperature data are less reliable because of an unexpectedly large measured inlet carbon tetrachloride concentration of 19,000 ppm. This upset undoubtedly increased the first thermal wave peak temperature. Hence, this temperature was discarded from the analysis. The inlet concentration was immediately adjusted to 5,000 ppm, and it is presumed that subsequent peaks represent the expected response.

Peak temperature rises for the second, third, and fourth thermocouples were 34 °F, 22 °F, and 22 °F. This computes to an average peak temperature rise of 26 °F. No wave travel rate was calculated since the initial high concentration would alter all subsequent rate calculations.

These tests indicate that at carbon tetrachloride concentrations of 5,000 ppm, the presence of 200 ppm, of MEK raises the peak temperatures by about 2 °F.

TEST 5

Test 5 was run at an inlet carbon tetrachloride concentration of 10,000 ppm, and a superficial velocity of 40 ft/m (500 ft³/min production). Total test time was 2.0 h. Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the GAC surface.

The peak temperature rises and associated times for the first four thermocouples were 52 °F at 28 min, 58 °F at 50 min, 54 °F at 70 min, and 53 °F

at 90 min. This computes to an average peak temperature rise of 56 °F and thermal wave rate of travel of 8.9 in./h.

TEST 6

Test 6 was run at an inlet carbon tetrachloride concentration of 20,000 ppm, and a superficial velocity of 40 ft/m (500 ft³/min production). Total test time was 2.6 h. Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the GAC surface.

The peak temperature rises and associated times for the first four thermocouples were 112 °F at 14 min, 137 °F at 24 min, 137 °F at 31 min, and 133 °F at 42 min. This computes to an average peak temperature rise of 130 °F and thermal wave rate of travel of 18.2 in./h.

TEST 7

Test 7 was run at an inlet carbon tetrachloride concentration of 30,000 ppm, and a superficial velocity of 40 ft/m (500 ft³/min production). Total test time was 1.7 h. Temperatures were measured at 3.5, 7.0, 10.5, and 14.0 in. from the GAC surface.

The peak temperature rises and associated times for the first four thermocouples were 140 °F at 14 min, 158 °F at 22 min, 167 °F at 25 min, and 166 °F at 36 min. This computes to an average peak temperature rise of 153 °F and thermal wave rate of travel of 22.5 in./h.

Figure D.5-4. GAC Column Bench-Scale Phase I-Test 1 Temperature Versus Time.

Figure D.5-6. GAC Column Bench-Scale Phase I-Test 3 Temperature Versus Time.

D.5-20

Figure D.5-7. GAC Column Bench-Scale Phase I-Test 4 Temperature Versus Time.

Figure D.5-8. GAC Column Bench-Scale Phase I-Test 5 Temperature Versus Time.

Figure D.5-9. GAC Column Bench-Scale Phase I-Test 6 Temperature Versus Time.

Figure D.5-10. GAC Column Bench-Scale Phase I-Test 7 Temperature Versus Time.

ATTACHMENT D.6

BENCH-SCALE ADSORBER TESTS
PHASE II TESTING
NOVEMBER 8 TO NOVEMBER 19, 1993

PHASE II LABORATORY BENCH-SCALE TESTING OF GAC ADSORPTION

SUMMARY

From November 8 to November 19, 1993, the Phase II GAC column bench-scale tests were conducted at the Department of Civil and Environmental Engineering at Washington State University. These tests were performed as a followup to the Phase I testing that took place in August 1993. The purpose of the tests was threefold: (1) to provide experimental data that directly relates to operation of a field VES at concentrations of 10,000 ppm_v of carbon tetrachloride with other solvents present, (2) to determine if high concentrations of carbon tetrachloride adsorbing onto GAC without the presence of other solvents could have caused the temperature rises seen during the overheating incident, and (3) to implement and test heat suppression methods that are suitable for field use.

The following changes were incorporated into the test equipment setup used in the Phase I testing: (1) additional thermocouples, (2) multiple solvent dosing, and (3) heat suppression methods. The thermocouples were added in a horizontal array located at the 28-in. level. The array consisted of a thermocouple located in the center of the column, a thermocouple located halfway between the center and the wall (quarter-diameter point), and a thermocouple located halfway between the quarter-diameter thermocouple and the wall (eighth-diameter point). This array provided temperature measurements radially from the center to the wall of the column. The capability to introduce additional solvents to the main air stream allowed the injection of methylene chloride and chloroform as well as carbon tetrachloride and MEK. Two heat suppression methods were incorporated into the system. The first allowed the system to be flushed with nitrogen gas, replacing the oxygen in the column, and the second allowed the column to be flooded with water.

Tests 1 through 3 were operated at a nominal carbon tetrachloride concentration of 10,000 ppm_v with methylene chloride and chloroform present. The concentration of MEK was varied from 200 ppm_v to 1,000 ppm_v in these tests. The peak GAC temperatures observed during these tests did not exceed 155 °F and in general occurred in a narrow band for the duration of each test.

Test 4 involved the use of GAC that had been prewetted with water in an effort to reduce the temperatures in the GAC. While this method showed promise in that the observed temperature rises were about 10 °F less than an equivalent test using dry GAC, there were a number of unknowns involved, and further testing should be done if this method is to be implemented.

Tests 5 and 6 were operated at nominal concentrations of 40,000 ppm_v and 55,000 ppm_v of carbon tetrachloride, respectively, and without any other solvents present in the airflow stream. The peak GAC temperatures observed in these tests were about 473 °F and 445 °F, respectively. These temperatures are well below the temperatures reached during the overheating incident, indicating that the heat generated by carbon tetrachloride adsorption alone did not cause the incident.

The spent GAC after each test was tested for pH, with results ranging from 9.18 to 10.13. The carbon tetrachloride hydrolysis reaction produces

hydrochloric acid, which would lower the pH of the GAC. The results of the pH testing indicate that little if any hydrolysis occurred because the pH of virgin GAC is approximately the same as the spent GAC used in the tests.

TEST EQUIPMENT SETUP

The test equipment setup is shown in Figure D.6-1. The setup consists of a gas inlet stream preparation area, a GAC-filled column, an offgas adsorber, heat suppression equipment, and a data acquisition system.

1. Inlet Stream Preparation

A small laboratory blower was used to force the main ambient air stream through the GAC-filled column. The main air stream was dosed with controlled amounts of solvents to provide the required mixture at the inlet of the column.

The dosing apparatus was set up in a laboratory hood. It consisted of a source of forced air, flasks of liquid solvents, a water bath, and appropriate tubes and valves. The required solvents were placed in flasks, which were then placed in the water bath. Experience from the Phase I testing showed that the temperatures of the solvents significantly affected the rate at which they volatilized, and that the temperatures of the solvents dropped as the evaporation process occurred. Maintaining steady temperatures in the water baths contributed to keeping constant inlet solvent concentrations. Air was forced through the flasks at a controlled rate via the use of sensitive valves. The effluent stream of each flask was then fed into the main air stream, where mixing and dilution to required levels took place.

The inlet solvent concentrations were monitored periodically throughout each test. Samples were collected in a gas collection bag and concentration levels were measured offline by an analytical meter. As needed, the solvent feed flows were adjusted to maintain the proper concentrations.

2. Test Column

The test column consisted of a 6-ft long, 3-in.-diameter steel pipe. A 3-in. tee was attached at each end with one leg blanked so that the flow stream made right angle turns entering and exiting the column. Instrumentation and sample ports were provided throughout the length of the column, and are summarized in Table D.6-1. Additional valves and connections for the heat suppression methods were located at the inlet and outlet tees. The column was surrounded by a molded sleeve of 1-in.-thick fiberglass insulation. The inside wall of the pipe was coated with a temperature and chemically resistant paint to preclude the presence of iron, which is known to catalyze the hydrolysis reaction of carbon tetrachloride.

Literature reports and a telephone conversation with a national GAC expert and published experimentalist confirmed the validity of the design of the column for the planned testing. With adequate insulation to minimize wall heat loss, such a configuration is directly scaleable to the field GAC canisters.

Figure D.6-1. Test Equipment Setup.

Table D.6-1. Phase II Testing Instrument Locations.

Ch.	Instrument	Designation	Location
1	Flowmeter	Flow	Prior to inlet tee
2	Humidity gage	Inlet Hum	Ambient
3	Humidity gage	Outlet Hum	Outlet tee
4	Humidity gage	Inlet Hum Temp	Ambient
5	Humidity gage	Outlet Hum Temp	Outlet tee
6	Thermocouple	Inlet TC	Inlet tee
7	Thermocouple	Outlet TC	Outlet tee
8	Thermocouple	Exterior TC	28 in. down, on pipe exterior
9	Thermocouple	1/8 Diameter	28 in. down, at the 1/8 diameter
10	Thermocouple	1/4 Diameter	28 in. down, at the 1/4 diameter
11	Thermocouple	3½ in. TC	3½ in. down, center of column
12	Thermocouple	7 in. TC	7 in. down, center of column
13	Thermocouple	10½ in. TC	10½ in. down, center of column
14	Thermocouple	14 in. TC	14 in. down, center of column
15	Thermocouple	17½ in. TC	17½ in. down, center of column
16	Thermocouple	21 in. TC	21 in. down, center of column
17	Thermocouple	24½ in. TC	24½ in. down, center of column
18	Thermocouple	28 in. TC	28 in. down, center of column
19	Thermocouple	35 in. TC	35 in. down, center of column
20	Thermocouple	42 in. TC	42 in. down, center of column
21	Thermocouple	49 in. TC	49 in. down, center of column
22	Thermocouple	56 in. TC	56 in. down, center of column
23	Thermocouple	63 in. TC	63 in. down, center of column
24	Thermocouple	70 in. TC	70 in. down, center of column
25	Thermocouple	Ambient TC	Ambient
26	Thermocouple	Bath TC	Water bath
N/A	Sample port	Inlet Port	Inlet tee
N/A	Sample port	1 ft Port	1 ft down from top of column
N/A	Sample port	5 ft Port	5 ft down from top of column
N/A	Sample port	Outlet Port	Outlet tee

The test column held approximately 9 lb of virgin GAC. The column was loaded with virgin GAC prior to each test, except for Test 3, which used the same GAC used in Test 2.

3. Offgas Adsorber

The exit stream from the column was connected by a 2-in. flexible hose to an offgas adsorber located in the exhaust hood. The offgas adsorber was loaded with GAC to adsorb any solvent vapors that may have escaped the column. The exhaust from the offgas adsorber was discharged to the laboratory hood.

4. Heat Suppression Methods

The GAC-filled column was configured with two methods of heat suppression. The first consisted of a pressurized tank of nitrogen gas connected to the column. In the event an excessive temperature rise was encountered, the adsorption test would be ceased and the column flushed with nitrogen gas, forcing the solvent vapors and oxygen out, thereby stopping any combustion that may be occurring. The second heat suppression method consisted of an elevated tank of water connected to the column. The water would be used to flood the column, stopping any reactions occurring and acting as a heat sink to lower the temperatures within the column.

In both methods, the suppression medium was connected to the outlet tee at the base of the column. Valves were arranged such that the inlet air stream could be shut down, the inlet switched to the offgas adsorber, the outlet stream closed, and the suppression medium introduced into the outlet tee. This would result in the suppression medium flushing the column from the bottom to the top, and the exiting vapors being directed through the offgas adsorber.

5. Data Acquisition System

Air stream flow rates, humidities, and temperatures were automatically recorded by a data acquisition system. Two dataloggers were used in parallel to monitor a total of 26 data channels. These channels are listed in Table D.6-1. Data were recorded every minute. In addition, data from 16 selected channels were displayed on a video monitor in real time, allowing visual monitoring of critical information.

Sampling of the air stream for solvent concentrations was performed periodically throughout each test. Sample ports were located at the inlet tee, 1 ft below the top of the GAC, 5 ft below the top of the GAC, and at the outlet tee. Sampling was done by bleeding air from the sample port into a gas collection bag which was then connected to an IR analytical meter. Solvents tested for and the range over which the meter was factory calibrated are given in Table D.6-2.

Table D.6-2. IR Analytical Meter Calibration.

Solvent	Calibrated range (ppm _v)
CCl ₄	118 - 114,006
MEK	106 - 11,424
CH ₂ Cl ₂	148 - 9,593
CHCl ₃	47.1 - 1,163
Water	--

TEST PLAN

The tests were designed to (1) gather data on the operation of a VES at concentrations of 10,000 ppm_v carbon tetrachloride with other solvents present, (2) determine if high concentrations of carbon tetrachloride adsorbing onto GAC without the presence of other solvents could have caused the temperature rises seen during the overheating incident, and (3) test heat suppression methods that are applicable to field use. The conditions for each test are shown in Table D.6-3.

Table D.6-3. Bench-Scale Column Phase II Test Plan.

Test	Inlet concentration (ppm _v)				Other conditions
	CCl ₄	MEK	CH ₂ Cl ₂	CHCl ₃	
1	10,000	200	200	500	
2	10,000	500	200	500	Run until 28 in. TC peaks; do not change GAC following test
3	10,000	1,000	200	500	Continue using GAC from prior test after allowing time to cool
4	10,000	200	200	500	Prewet the GAC
5	40,000	--	--	--	
6	55,000	--	--	--	

All of the tests were performed with an air stream superficial velocity of 40 ft/min through the bench-scale column, which corresponds to the 500-ft³/min design limit of the field canisters. All tests were run under ambient conditions of 70 °F and approximately 40% humidity.

Following each test except Test 2, the column was emptied and refilled with fresh GAC. A sample of the spent GAC from each test was tested for pH using an industry-accepted standard method. The GAC sample taken following Test 3 was a mixed sample of GAC loaded during Tests 2 and 3.

In addition to performing the above tests, the possibility of an excessive temperature rise was considered in the safety plan governing the

performance of these tests. In such an event, the flow of solvents would be shut down first, leaving the main air stream on and flushing the column with ambient air. If the observed temperatures did not decrease, the column would be flushed with nitrogen. If the temperatures still did not decrease, the column would be filled with water.

TEST RESULTS

A description of each test follows.

Test 1: 10,000 ppm_v CCl₄, 200 ppm_v MEK, 200 ppm_v CH₂Cl₂, 500 ppm_v CHCl₃

This test was run to saturation to provide a baseline of comparison for the other tests and provide data on target operating conditions. The test ran approximately 9 h and saturated the entire column. The maximum temperature recorded was 153.4 °F. This represents about an 80 °F temperature rise. Successive temperature peaks do not show an increasing pattern, but rather that a temperature plateau is reached, as seen in Figure D.6-2.

Test 2: 10,000 ppm_v CCl₄, 500 ppm_v MEK, 200 ppm_v CH₂Cl₂, 500 ppm_v CHCl₃

Test 2 was not run to saturation. The 28-in. thermocouple was closely monitored, and when it peaked, the test was stopped. All flows, solvent and main air were turned off. The maximum temperature recorded was 153.2 °F, essentially the same as the previous test. Successive peaks GAC temperature peaks (17½ in., 21 in., 24½ in., and 28 in.), as seen in Figure D.6-3, indicate that a plateau was reached.

Test 3: 10,000 ppm_v CCl₄, 1000 ppm_v MEK, 200 ppm_v CH₂Cl₂, 500 ppm_v CHCl₃

Test 3 did not begin with fresh GAC, but continued where Test 2 left off, to simulate a shutdown and restart in the field. The temperature peaks seen in Figure D.6-4 during this test are low and come in rapid succession while the mass transfer zone moves through the previously saturated GAC, then reverts to previously observed behavior. The maximum temperature recorded was 164.7 °F, corresponding to a temperature rise of about 95 °F. As in Tests 1 and 2, a temperature plateau was reached.

Test 4: 10,000 ppm_v CCl₄, 200 ppm_v MEK, 200 ppm_v CH₂Cl₂, 500 ppm_v CHCl₃,
310 mL H₂O prewetting

Prior to initiation of this test, 310 mL of water was poured into the top of the test column, soaking the GAC. Slight temperature increases were noted as the water penetrated the GAC bed, down to about the 21-in. level. The temperature peaks recorded during the adsorption test are significantly lower in this region, but gradually increase as the adsorption front moves through the bed. The highest temperature recorded is about 143 °F, as seen in Figure D.6-5, or about a 75 °F temperature rise. The temperature plateau seen in this test is about 10 °F lower than the plateaus seen in previous tests.

Figure D.6-2. Bench-Scale Column Phase II Test 1 Peak Temperatures and Profile at 3 Hours.

Figure D.6-3. Bench-Scale Column Phase II Test 2 Peak Temperatures and Profile at 2 Hours.

Figure D.6-4. Bench-Scale Column Phase II Test 3 Peak Temperatures and Profile at 2 Hours.

Figure D.6-5. Bench-Scale Column Phase II Test 4 Peak Temperatures and Profile at 4 Hours.

Test 5: 40,000 ppm_v CCl₄

This test was conducted at a higher concentration of carbon tetrachloride but with no other compounds in the airstream. Immediately after the 17½-in. thermocouple peaked at 375 °F, the flow of carbon tetrachloride was stopped for about 7 min, leaving the main flow of ambient air on. The temperature at the 17½-in. thermocouple fell 180 °F during this time. Flow of carbon tetrachloride was restarted and the test continued until after the 56-in. thermocouple had peaked. The highest temperature recorded during the test was 473.5 °F, as seen in Figure D.6-6, representing a 405 °F temperature rise.

Test 6: 55,000 ppm_v CCl₄

This test was conducted at the highest inlet carbon tetrachloride concentrations to date. The concentration level was difficult to hold steady at anything above about 40,000 ppm_v, and actual measured concentrations during this test range from 47,400 ppm_v to 64,500 ppm_v. Peak temperatures during this test tended to be somewhat below those measured in the prior test. The maximum temperature recorded during the test was 445 °F, as seen in Figure D.6-7, representing a temperature rise of 375 °F.

Data Analysis

In general, the thermal wave rate of travel from one thermocouple to the next is not necessarily a constant, and it clearly increases as the inlet concentration increases. Also, the temperature gradients vertically through the column become steeper as the inlet concentrations rise. The heat suppression methods were never required and, therefore, not tested.

Table D.6-4 summarizes the technical data resulting from each of the tests performed. The rate of loading of the solvents is calculated from the average inlet concentration and the rate of air flow. The loading ratio is calculated from the rate of loading, the measured velocity of the temperature wave through the GAC column, and the known density of GAC. The total loading is the product of the rate of loading and the duration of the test.

The data gathered show that the generated heat is related to inlet concentration. Figure D.6-8 summarizes the maximum peak temperatures observed during both the Phase I and Phase II testing. The relationship between the inlet concentration and temperature appears to be nearly linear up to 30,000 ppm_v of carbon tetrachloride. Beyond this point, the relationship is less clear.

The observed GAC temperature plateau achieved in Test 6 was below that of Test 5, despite the fact that Test 6 was conducted with a higher inlet concentration of carbon tetrachloride. We are unable to offer an explanation at this time, except to note that steady-state conditions may not have been reached during this test. At steady state, peak temperatures may have been similar in the two tests, indicating that the peak temperature of about 450 °F may represent the point at which the rate of adsorption and desorption are

Figure D.6-6. Bench-Scale Column Phase II Test 5 Peak Temperatures and Profile at 56 Minutes.

Figure D.6-7. Bench-Scale Column Phase II Test 6 Peak Temperatures and Profile at 38 Minutes.

Table D.6-4. Bench-Scale Column Phase II Testing Summary.

Test	Superficial velocity (ft/min)	Duration of tests (h)	Solvent properties	Solvents				Peak temp (°F)	Temp wave rate (in./h)	Measured pH
				CCl ₄	MEK	CH ₂ Cl ₂	CHCl ₃			
1	40	9.00	Average concentration (ppm _v)	9,096	177	170	570	153.4	9.3	9.18
			Rate of loading (lb/h)	0.466	0.004	0.005	0.023			
			Loading ratio (lb solvent/lb GAC)	0.411	0.004	0.004	0.020			
			Total loading (lb)	4.195	0.038	0.043	0.204			
2	40	3.05	Average concentration (ppm _v)	9,161	518	250	578	153.2	9.2	10.01 ^a
			Rate of loading (lb/h)	0.469	0.012	0.007	0.023			
			Loading ratio (lb solvent/lb GAC)	0.418	0.011	0.006	0.020			
			Total loading (lb)	1.432	0.038	0.022	0.070			
3	40	2.93	Average concentration (ppm _v)	10,430	1,004	201	191	164.7	10.2	10.01 ^a
			Rate of loading (lb/h)	0.534	0.024	0.006	0.008			
			Loading ratio (lb solvent/lb GAC)	0.430	0.019	0.005	0.006			
			Total loading (lb)	1.568	0.071	0.017	0.022			
4	40	8.63	Average concentration (ppm _v)	10,465	231	256	550	141.9	9.4	9.56
			Rate of loading (lb/h)	0.536	0.006	0.007	0.022			
			Loading ratio (lb solvent/lb GAC)	0.469	0.005	0.006	0.019			
			Total loading (lb)	4.629	0.048	0.063	0.189			
5	40	1.78	Average concentration (ppm _v)	40,037	--	--	--	473.5	32.0	10.13
			Rate of loading (lb/h)	2.05	--	--	--			
			Loading ratio (lb solvent/lb GAC)	0.52	--	--	--			
			Total loading (lb)	3.66	--	--	--			
6	40	0.78	Average concentration (ppm _v)	55,966	--	--	--	444.7	46.7	9.59
			Rate of loading (lb/h)	2.77	--	--	--			
			Loading ratio (lb solvent/lb GAC)	0.48	--	--	--			
			Total loading (lb)	2.17	--	--	--			

^aTests 2 and 3 used the same GAC. Following Test 3, the GAC was mixed and a single pH measurement made.

Figure D.6-8. Observed Bench-Scale Test GAC Peak Temperatures Versus Carbon Tetrachloride Concentration--500 ft³/min Equivalent Flow.

approximately equal, resulting in essentially no further heating. A second possibility is that a limited exothermic reaction other than adsorption of carbon tetrachloride occurred during Test 5 that was sufficient to increase the temperatures within the GAC without triggering an excessive temperature rise.

The horizontal thermocouple array located at the 28-in. depth in the GAC column provided data on the shape of the thermal wave front. The array was composed of four thermocouples. The 28-in. thermocouple was located at the cross-sectional center of the GAC column, the 1/4-diameter and 1/8-diameter thermocouples were located in line between the center and the wall, and the exterior thermocouple was located on the exterior of the pipe but inside the insulation. The resulting data from Tests 1 and 5 are plotted in Figures D.6-9 and D.6-10, respectively. Figure D.6-9 shows that the GAC temperature profile at the 28-in. depth is flat across the center of the column with a drop in temperature near the wall of the column. The flat region is presumed to be nearly adiabatic and represents the maximum temperatures that can be expected under the conditions of inlet concentration of 10,000 ppm, carbon tetrachloride, an even flow pattern, and no exothermic reactions other than carbon tetrachloride adsorption occurring. The presence of flow channeling, oxidation, or hydrolysis would be expected to alter the horizontal temperature profile. The decrease in temperature near the column wall is attributed to heat loss into the column wall. As the GAC temperature falls below the wall temperature, some of the heat stored in the wall is returned to the GAC, as indicated by higher temperatures near the wall than in the center of the column after the thermal wave passed the 28-in. depth. Figure D.6-10 shows that for the higher temperatures produced by adsorption of higher concentrations of carbon tetrachloride, the region of wall loss extends further into the column and the centerline where peak temperatures are measured may no longer be near adiabatic conditions.

An additional factor is the base temperature, or the temperature within the GAC column prior to a temperature rise. The base temperature is affected by ambient conditions. All of the Phase II tests were performed with an ambient temperature of about 70 °F. Increasing the ambient temperature would likely increase the temperatures in the GAC by an equivalent or slightly less amount. The change in GAC temperature may not equal the change in the ambient temperature because as temperatures rise, desorption increasingly occurs, which provides a damping effect due to the endothermic nature of desorption.

An additional aspect of the base temperature is the temperature of the GAC at the beginning of adsorption. If normal extraction operation is interrupted and ambient air allowed to blow through the canister for a brief time, the heat of the thermal front will be distributed downstream, elevating the temperature of the GAC. When extraction operations resume, the peak temperatures may be higher than previously experienced because of the higher base temperature. The same result may occur if the GAC canister has been heated by solar radiation prior to extraction operations. It is recommended that prior to the initiation of any extraction operations, ambient air be forced through a canister for a sufficient length of time, based on operational experience, to ensure that the GAC temperatures are uniformly within desired operational limits.

Figure D.6-9. Bench-Scale Column Phase II Test 1 Horizontal Temperature Profile.

Figure D.6-10. Bench-Scale Column Phase II Test 5 Horizontal Temperature Profile.

D.6-21

Bench-Scale Performance at 10,000 ppm_v of Carbon Tetrachloride

The temperatures generated by operating the test column with 10,000 ppm_v of carbon tetrachloride are comfortably below the any of the published oxidation or combustion temperatures, as shown in Figure D.6-11. At a carbon tetrachloride concentration of 10,000 ppm_v and with no other solvents present, the peak observed temperature was 130 °F. Addition of MEK, methylene chloride, and chloroform resulted in observed temperatures of about 153 °F for the 200 ppm_v and 500 ppm_v MEK cases, and about 165 °F in the 1,000 ppm_v MEK case.

These data are directly relatable to the field VES extraction operating at 500 ft³/min of 70 °F inlet flow and a inlet concentration of 10,000 ppm_v of carbon tetrachloride.

Test 2 was run until the 28-in. thermocouple peaked, then all flows were halted. The column was allowed to cool overnight. Test 3 was performed the following day using the same GAC. This simulates a shutdown and restart of a field canister. The peak temperature profiles show the thermal wave front rapidly moved through the first 28-in., or the region of saturated GAC, without significant temperature rises, then once it entered the unsaturated GAC, the expected pattern of temperature peaks was seen. Based on this, there appear to be no negative effects from stopping extraction operations and restarting using the same canister. This conclusion is based on the premise that no hot spots are generated within the GAC due to the absence of the cooling effect of gas flowing through the GAC. Such hot spots could be kindled into more rapid combustion once the flow of air is resumed.

Heat Suppression Methods

The heat suppression methods configured into the bench-scale test were never utilized. None of the tests performed, including those operating at elevated carbon tetrachloride concentrations, initiated excessive temperature rise. It is possible that such a condition could be created by including MEK or other solvent in an elevated carbon tetrachloride concentration inlet stream. However, the heat of oxidation for MEK is large enough that if the MEK begins to oxidize, the temperatures within the GAC column may exceed the threshold of hydrolysis. This presents a risk of phosgene generation, and suitable detectors should be acquired prior to such a test.

During Test 5, the flow of solvents was shut off for a period of 7 min while the main air flow continued. The temperature at the 17½-in. thermocouple dropped 180 °F before the flow of solvents was restarted. This demonstrates that running ambient air through a GAC canister is an effective method of lowering high temperatures if there are no heat-generating reactions occurring. This method should be considered prior to terminating GAC loading operations for periods of several hours or more.

One possible method of limiting the temperatures within the column before an excessive temperature rise is initiated is to prewet the GAC. This was done for Test 4 by pouring 310 mL of water into the top of the column after the GAC had been loaded. The results of this test show lower temperatures and slowly increasing peak temperatures over the first five

Figure D.6-11. Summary of Temperatures Relating to Overheating Incident.

probable minimum GAC temperatures achieved in overheating incident:

thermocouples (up to the 17½-in. thermocouple), to a peak temperature plateau. The peaks are approximately 10 °F lower than the peaks of an equivalent test without prewetting (Test 1). Also, there appears to be more heat carried with the airstream since the temperatures recorded by thermocouples downstream of the thermal front are higher than in other tests. These results indicate that prewetting has a small impact on limiting temperatures in a GAC canister. Table D.6-4 indicates that adsorption efficiency may be increased by more than 10% by prewetting, however.

Correlation of Bench-Scale Data to Field VES Operation

The bench-scale column was designed so that the data obtained from these tests are directly relatable to the larger field VES units. During the design process, a published researcher who has done experimental work in the investigation of carbon bed fires was contacted for advice on test equipment sizing and test procedures. He suggested a column height identical to the field canister height, with adequate insulation to minimize wall heat losses. A 3-in.-diameter pipe was deemed suitable for the test. The thermal wave rate and the loading data given here should be representative of data for the case of a field canister operating at 500-ft³/min flow and similar inlet concentrations. Peak temperatures should also be representative for reasons previously discussed.

Wall flow effects can potentially become a factor in scale-up. Wall flow bypassing GAC results in producing larger than expected outlet carbon tetrachloride concentrations. An accepted rule of thumb is that wall flow is negligible if the pipe diameter is a minimum of 10 times the diameter of an average particle, which is the case for the bench-scale testing. The factor is 18 times for this apparatus. Additionally, sampling of the outlet air stream revealed minimum breakthrough of carbon tetrachloride. Thus, it is concluded that there were no appreciable wall flow effects.

ATTACHMENT D.7
CANISTER PAINT COUPON TESTING

ATTACHMENT D.7
CANISTER PAINT COUPON TESTING

Three paint coupons were tested for paint discoloration during heating. Squares of 1/4-in.-steel, identical to the canister material, were painted with exterior canister paint and with interior canister epoxy. In addition, 1-in. drain plugs were taken from canisters that were weathered in the field. The coupons were placed in an air-atmosphere oven and the temperature was increased in a stepwise fashion. After contacting the pieces at a desired temperature for 1 h, they were removed from the oven and pictures were taken. Baseline test pieces (unheated) were used in the pictures for comparative purposes. The oven was allowed to equilibrate to a new set point and the pieces were returned for heating. This process continued to a temperature of 750 °F. An additional test was performed to evaluate if the paint on the test pieces underwent any changes during the stepwise heating process that would not be reflected if the piece was brought to an elevated temperature of 550 °F in one step. The test pieces (interior epoxy and weathered paint) brought to temperature in this fashion were slightly darker in color compared to the pieces brought up to 550 °F in a stepwise fashion. There was no detectable color difference for the exterior paint coupon.

Table D.7-1 summarizes the visual observation taken at each temperature.

Table D.7-1. Visual Observations of Paint Discoloration During Stepwise Heating. (sheet 1 of 2)

Test piece	Description
270 °F	
Exterior paint	No detectable difference
Interior epoxy	Slight darkening
Weathered paint	No detectable difference
300 °F	
Exterior paint	Very slight darkening
Interior epoxy	Notable yellowing
Weathered paint	No detectable difference
375 °F	
Exterior paint	Lighter in color
Interior epoxy	Darker in yellow
Weathered paint	Lighter in color
420 °F	
Exterior paint	Light tan color
Interior epoxy	Dark brown
Weathered paint	Lighter color
465 °F	
Exterior paint	Darker tan color
Interior epoxy	Darker brown
Weathered paint	Brown-gray color
520 °F	
Exterior paint	Dark tan/brown
Interior epoxy	Very dark brown - paint separated from coupon
Weathered paint	Taken on a "burned" appearance
550 °F	
Exterior paint	Darker tan
Interior epoxy	More extensive bubbling of paint
Weathered paint	Darker in color

Table D.7-1. Visual Observations of Paint Discoloration During Stepwise Heating. (sheet 2 of 2)

Test piece	Description
660 °F	
Exterior paint	Chocolate brown, no cracking
Interior epoxy	
Weathered paint	Darker chocolate brown, slight cracking
710 °F	
Exterior paint	Black to dark brown, slight cracking
Interior epoxy	
Weathered paint	Black to dark brown, peeled and cracked
750 °F	
Exterior paint	Black, peeled and cracked
Interior epoxy	
Weathered paint	Black, peeled and cracked

APPENDIX E

CANISTER OVERHEATING INCIDENT
HEAT TRANSFER MODELING

CONTENTS

E.1.0	INTRODUCTION	E-1
E.2.0	BACKGROUND HISTORY	E-1
E.2.1	SUMMARY OF VAPOR EXTRACTION TECHNOLOGY AT THE HANFORD SITE	E-1
E.2.2	DESCRIPTION OF THE INCIDENT	E-2
E.2.3	COMPARISON WITH LOW INLET CONCENTRATION CASE	E-4
E.2.4	POST-INCIDENT ANALYSES	E-5
E.2.4.1	Paint Discoloration Testing	E-5
E.2.4.2	Bench-Scale Adsorption Testing	E-5
E.2.4.3	Full-Scale Thermocouple Response Tests	E-9
E.2.4.4	Thermogravimetric Analysis of GAC and Carbon Tetrachloride	E-9
E.2.4.5	Acid Formation Testing	E-11
E.2.4.6	Potential Phosgene and Hydrochloric Acid Creation	E-12
E.3.0	MODEL DEVELOPMENT	E-13
E.3.1	PURPOSE OF MODELING	E-13
E.3.2	DISCUSSION OF MECHANISMS	E-14
E.3.3	THERMAL MODELING DEVELOPMENT	E-16
E.3.3.1	Overall Energy Balance	E-16
E.3.3.2	Deadzone Analysis	E-17
E.3.3.3	Uniform Heat Distribution Model	E-18
E.3.3.4	Stacked Heat Distribution Model	E-19
E.3.3.5	Conductive/Convective Model Limitations	E-19
E.3.3.6	Additional Adsorption Following the Thermal Wave	E-19
E.3.3.7	Impact of Carbon Tetrachloride, Trace Organics, and GAC Reactions	E-20
E.4.0	MODELING BASES AND ASSUMPTIONS	E-21
E.4.1	GAC SYSTEM PARAMETERS	E-21
E.4.2	GAC ISOTHERM CURVES	E-21
E.4.3	CALCULATION OF HEAT OF ADSORPTION	E-21
E.4.4	GAC LOADING VARIABILITY	E-25
E.5.0	ANALYSIS AND MODELING RESULTS	E-31
E.5.1	OVERALL ENERGY BALANCE	E-31
E.5.2	DEADZONE ANALYSIS	E-37
E.5.3	CONDUCTIVE/CONVECTIVE MODEL LIMITATIONS	E-38
E.5.4	ADDITIONAL ADSORPTION FOLLOWING THE THERMAL WAVE	E-39
E.5.5	IMPACTS OF CARBON TETRACHLORIDE REACTIONS	E-42
E.5.6	IMPACTS OF TRACE ORGANICS	E-44
E.5.7	IMPACTS OF GAC COMBUSTION	E-45
E.5.8	CARBON TETRACHLORIDE CONCENTRATION THROUGH GAC BED	E-46
E.6.0	CONCLUSIONS AND RECOMMENDATIONS	E-48
E.6.1	CONCLUSIONS	E-48
E.6.2	RECOMMENDATIONS	E-50
E.7.0	REFERENCES	E-51

CONTENTS (cont.)

FIGURES:

E-1	Bench-Scale Phase I Test Equipment Schematic	E-6
E-2	Temperature Curves for GAC-Filled Column Bench-Scale Test at 10,000 ppm _v Carbon Tetrachloride	E-8
E-3	Thermocouple Response Test: GAC Temperature Versus Time	E-10
E-4	Vendor-Supplied Isotherm Plot for Carbon Tetrachloride Adsorption on GAC	E-24
E-5	Predicted Heat of Adsorption Versus GAC Loading	E-26
E-6	Observed GAC Loading Versus Inlet Carbon Tetrachloride Concentration	E-27
E-7	Observed Bench-Scale Test GAC Temperature Rise Versus Carbon Tetrachloride Concentration	E-29
E-8	Maximum GAC Temperature as a Function of Inlet Carbon Tetrachloride Concentration	E-30
E-9	Temperature Profiles for GAC-Filled Column Bench-Scale Test at 30,000 ppm _v Carbon Tetrachloride	E-34
E-10	Contribution of Energy Balance Components Relative to Carbon Tetrachloride Heat of Adsorption	E-36
E-11	Calculated GAC Particle Surface Temperature Versus Time	E-40
E-12	Calculated GAC Particle Heat Loss Versus Time	E-41
E-13	Calculated Bench-Scale Test Carbon Tetrachloride Concentration in GAC Bed and Observed Temperature Profiles Versus GAC Depth	E-47
E-14	Summary of Temperatures Related to Overheating Incident	E-49

TABLES:

E-1	Comparison of High and Low Carbon Tetrachloride Loading Rate Cases	E-4
E-2	GAC Heat Modeling Parameters	E-22
E-3	Carbon Tetrachloride Heat Modeling Parameters	E-22
E-4	Process Parameters for Overheating Incident and Bench-Scale Test	E-23

CONTENTS (cont.)

TABLES (cont.):

E-5	Carbon Tetrachloride Heat of Adsorption as a Function of GAC Loading	E-25
E-6	Adsorption Parameters as a Function of Inlet Carbon Tetrachloride Concentration	E-28
E-7	Energy Balance for Bench-Scale Test at 30,000 ppm, Carbon Tetrachloride and Overheated Canister	E-32
E-8	GAC-Filled Column Bench-Scale Test at 30,000 ppm, Carbon Tetrachloride: Temperature Summary for Energy Balance	E-33
E-9	Reaction Heat Release and Relative Temperature Rises	E-43

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LIST OF ACRONYMS

CCl ₄	carbon tetrachloride
CHCl ₃	chloroform
CH ₂ Cl ₂	methylene chloride
COCl ₂	phosgene
DTA	differential temperature analyzer
GAC	granular activated carbon
HCl	hydrochloric acid
HEPA	high-efficiency particulate air
MEK	methyl ethyl ketone (C ₄ H ₈ O)
MS	mass spectrometer
MTZ	mass transfer zone
ppm _v	parts per million by volume
VES	vapor extraction system
TGA	thermogravimetric analyzer
WSU	Washington State University

E.1.0 INTRODUCTION

This appendix contains a thermal analysis of an overheating incident involving a canister filled with granular activated carbon (GAC). The GAC-filled canister was part of a treatment train used to adsorb carbon tetrachloride (CCl_4) vapors from a subsurface disposal site near the 216-Z-9 Trench in the 200 West Area of the Hanford Site. The overheating incident resulted in a band of discolored paint on the exterior surface of the canister. Although there was no other known damage to equipment, no injuries to operating personnel, and no releases of hazardous materials, the incident is of concern because it was not anticipated. It also represents the possibility of release of carbon tetrachloride and other hazardous vapors if the incident were to recur.

This appendix identifies and evaluates mechanisms that may affect temperatures within the GAC. These mechanisms are complex, highly interactive, and difficult to model as a system. Thus, the mechanisms most capable of contributing significantly to the overheating incident are analyzed individually or with limited interaction with other mechanisms. This analysis is intended to assist in the development of limits and controls to prevent recurrence of the incident.

E.2.0 BACKGROUND HISTORY

This section contains (1) a brief summary of the carbon tetrachloride vapor extraction technology, (2) a description of conditions surrounding the overheating incident, (3) a description of an earlier carbon tetrachloride extraction operation that resulted in a similar mass loading of carbon tetrachloride onto GAC without overheating, and (4) a summary of relevant analyses conducted to gain an understanding of the factors that contributed to the overheating incident.

E.2.1 SUMMARY OF VAPOR EXTRACTION TECHNOLOGY AT THE HANFORD SITE

Vapor extraction technology has been utilized as part of an Expedited Response Action to recover carbon tetrachloride from unsaturated sediments beneath the Hanford Site. Approximately 1,000 tons of carbon tetrachloride were disposed to three liquid waste disposal sites between 1955 and 1973. Most of the carbon tetrachloride is believed to remain in the unsaturated soils beneath the disposal sites: the 216-Z-1A Tile Field, the 216-Z-9 Trench and the 216-Z-18 Crib. The carbon tetrachloride can be recovered from the soil by extracting soil gas from wells drilled into the ground. A typical vapor extraction system (VES) at the Hanford Site consists of a cyclone to remove entrained water droplets that would otherwise damage downstream equipment, a heater to ensure that no mist is present that could blind the downstream high-efficiency particulate air (HEPA) filter, a blower with a capacity of up to 500 ft^3/min , a cooler to control the temperature of the air stream, three GAC-filled canisters in a series for adsorbing carbon tetrachloride and trace organics, and a stack for venting the treated soil gas to the atmosphere.

The first canister through which the extracted soil gas is passed is designated the "primary" canister. This canister is followed in the series by a "secondary" canister and then a "tertiary" canister.

Typically, a new canister is installed first in the tertiary position, from which it is moved stepwise to the primary position. After the primary canister is loaded with carbon tetrachloride it is removed from the treatment train for offsite reactivation. The former secondary canister is moved to the primary position, the tertiary canister is moved to the secondary position, and a fresh canister is moved to the tertiary position.

The primary canister used during the overheating incident had previously served as the secondary canister during characterization of soil gas at several other well locations. This canister is believed to have contained about 40 lb of carbon tetrachloride plus possible unknown compounds from the soil vapor when it was installed as the primary canister. A similar VES test was performed earlier in the day to characterize soil gas at a single well location. Less than 1 lb of carbon tetrachloride was collected in the primary canister during that characterization test.

Each of the three GAC-filled canisters used in the overheating incident contained about 1,760 lb of Envirotrol EI-410S 4 x 10 mesh virgin coconut shell-based GAC. The GAC bed within the canister is approximately 4 ft in diameter and 5.4 ft tall. The canisters are constructed of carbon steel that is painted on the exterior surfaces and coated with epoxy on the internal surfaces. An uncoated 20-mesh stainless steel screen supports the GAC bed inside each canister. The specifications for the exterior coating include a temperature resistance of 200 °F for both the primer (polyamide epoxy) and the paint (aliphatic polyurethane). The specifications for the interior coating (epoxy phenolic) indicate a temperature resistance of 225 °F.

E.2.2 DESCRIPTION OF THE INCIDENT

On the morning of June 3, 1993, one of the two VESs used at the Hanford Site was put into service to extract and treat soil gas from well 299-W15-32. The purpose of this work was to accurately characterize the carbon tetrachloride concentration of the soil gas in the vicinity of the well and gain an understanding of the flow characteristics of the well. Initial characterization of the well vapor samples had shown carbon tetrachloride concentrations ranging from 1,000 to 30,000 parts per million by volume (ppmv). Soil vapor from the well was being extracted and treated when the primary canister overheated. Overheating was discovered when an operator detected an abnormal odor and saw a narrow band of discolored paint on the exterior of the canister.

On detection of the overheated canister, the system blower was immediately shut down manually by a technician; this was followed by closure of the valve between the well and the blower. Air valves to the atmosphere were then opened upstream of the blower and downstream of the blower with the intent of allowing release of any pressurizing gas in the primary canister.

After shutdown of the VES was completed, emergency procedures were implemented. The Hanford Fire Department, among other organizations, was notified. After brief discussions about the nature of the overheated canister and its contents, fire department personnel began to spray the canister from

two sides with a water mist to cool it down. Shortly after the spraying operation commenced, a noncontacting infrared thermometer was used to monitor the temperature of the canister in the vicinity of the paint discoloration. This measurement was 240 °F and was the highest temperature recorded at any time during the incident. The canister temperatures measured at the same height but on the opposite side of the paint discoloration were equal to the ambient temperature.

After several sprayings, the canister valves were closed and the process hoses were removed from the primary canister and placed in plastic bags. The overheated canister was moved by forklift to the center of the site yard. The upper canister valve was then opened slightly, with a noticeable release of pressure. After about 4 h of spraying the external surface of the canister and taking temperature readings, the canister temperature appeared to stabilize at about 150 °F. The fire department personnel then departed.

Soon after the fire department personnel left the site, the VES technicians sensed that the external temperature of the canister was increasing. However, no quantitative measurements were made. Concurrently, discussions with a GAC manufacturer indicated that if the GAC inside the canister had reached ignition temperature, the only method for extinguishing oxidation of the GAC would be to fill the canister with water. Based on this advice and the best judgement of the project team, the decision was made to fill the canister with water. Thus, approximately an hour after the fire department personnel departed from the site, they were requested to return to fill up the canister with water. The noncontacting infrared thermometer indicated a temperature rise of about 10 °F since the previous measurement taken more than an hour before. This placed the surface temperature of the canister at about 160 °F.

The fire department personnel donned protective equipment and slowly fed water into the top inlet of the canister. The bottom outlet valve on the canister had been closed and capped. After about 40 min, the water level reached the top inlet and the water flow was shut off. According to the fire department, approximately 600 to 700 gal of water was pumped into the canister. The amount of water required to fill an empty canister to the level of the upper outlet is calculated to be about 605 gal. During the filling period, minor amounts of condensed water vapor were noted escaping from the top outlet. The area around the canister was cordoned off and safety personnel monitored the breathing zone for chlorinated hydrocarbons. None were detected. The fire department personnel again departed the site.

On June 7, approximately 350 gal of water was drained from the canister and placed into polyethylene-lined 55-gal drums. The pH of the water was measured because it was theorized that if the heat within the canister had been high enough to decompose the carbon tetrachloride, then hydrochloric acid (HCl) could have been produced. The measured pH of this drained water was between 0 and 1, indicating significant acidity. The pH of water extract from virgin carbon is about 9.5 according to vendor literature. An additional 20 gal of water was later drained from the canister and placed in a polyethylene-lined 55-gal drum.

The canister was refilled with water on June 8 to reduce the acidity and thus reduce the potential for corrosion of the canister itself. Approximately 350 gal of water was later removed and placed into polyethylene-lined 55-gal

drums. This water had a measured pH of 1.3. Samples of the drained water were taken on June 27 and analyzed for chloride and other anions associated with acid conditions. The analysis failed to detect chlorides and other anions at levels associated with strong acids. Thus, this analysis is considered potentially unreliable.

From June 25 through June 27, ambient air at about 500 stdft³/min was run through the overheated canister, followed by three other canisters in series. The purpose of this operation was to dry out the GAC to allow sampling. This effort proved to be successful in drying the GAC.

On June 27, the overheated canister was sampled, resulting in about 1 quart of GAC removed for analyses and for shipment to the GAC vendor for testing. Samples of GAC were taken along the central axis of the canister in the vicinity of the discolored paint. There was no visual evidence of oxidation in the retrieved samples.

On July 12, results of the testing of the GAC from the overheated area of the canister were received from the vendor. The GAC showed no evidence, neither physical nor chemical, of damage due to overheating.

E.2.3 COMPARISON WITH LOW INLET CONCENTRATION CASE

Between February 1992 and June 1993, a canister of the same type and size as used in the overheating incident was filled with carbon tetrachloride to about the same level as occurred in the incident. This operation, at the 216-Z-1A Tile Field, was without incident. The total heat added to the canisters due to the heat of adsorption was probably similar. Although the gas flow rates through the canisters were also approximately equal in the two cases, the concentrations of carbon tetrachloride in the gas and the volumes of gas passed through the canisters varied greatly. The key operating parameters of the overheating incident, which occurred at the 216-Z-9 Trench, are compared in Table E-1 to those of the case of low carbon tetrachloride gas concentrations, which occurred at the 216-Z-1A Tile Field. This comparison is made here to establish a foundation for bench-scale testing and thermal analyses reported in Sections E.2.4 and E.5.0 of this appendix.

Table E-1. Comparison of High and Low Carbon Tetrachloride Loading Rate Cases.

Parameter	Overheated canister (high CCl ₄ conc. @ 216-Z-9)	Similar canister (low CCl ₄ conc. @ 216-Z-1A)
Quantity of GAC/Canister	1,760 lb	1,760 lb
CCl ₄ Adsorbed	357 lb	~500 lb
VES Flow Rate	240 ft ³ /min	300 ft ³ /min
CCl ₄ Adsorption Rate	2.8 lb/min	0.072 lb/min
Total Air Flow	43,000 ft ³	2,090,000 ft ³

E.2.4 POST-INCIDENT ANALYSES

Several tests and analyses of the overheating incident have been made. This section contains a summary of these tests and analyses that are important to the thermal analyses reported in Section E.5.

E.2.4.1 Paint Discoloration Testing

The overheated canister shows a discolored streak at about 40% of the bed height. The roughly horizontal streak is about 8 in. wide and is about one-third the canister circumference in length. It varies in color from a "cocoa-brown" on the periphery to a "dark chocolate brown" at the assumed hottest spot. The darkest area is about 12 in. in length and is located approximately opposite the inlet and outlet ports of the canister. No peeling or blistering is evident in the discolored area.

The temperature of the discolored area had been measured at 240 °F shortly after the fire department personnel had begun to spray the canister with water to cool it down. Thus, uncertainty exists as to the actual temperature reached in the overheated area.

Tests were conducted to determine the temperatures required to achieve the "cocoa-brown" and "dark chocolate brown" colors. Testing involved the use of an electric oven open to the air to ensure oxidizing conditions. Coupons of steel painted with the same paint specified for coating both the exterior and interior surfaces of the canister, obtained from the canister manufacturer, were heated in the oven. A painted plug removed from another production canister was also heated in the oven with the coupons. The coupons and plug were heated in the oven at temperature steps for a period of 1 h at each temperature. The color changes observed for the exterior paint coupons closely matched those of the plug. This indicates that the exterior paint coupon is representative of the paint on the overheated canister. Testing showed that the temperatures that caused the "cocoa-brown" and "dark chocolate" discolorations were approximately 550 °F and 660 °F, respectively.

E.2.4.2 Bench-Scale Adsorption Testing

Bench-scale adsorption tests were conducted at Washington State University (WSU) in an attempt to simulate conditions that were observed in the overheated canister as well as those encountered during previous stable operations at the Hanford Site. The objective of the testing was to replicate the thermal conditions that led to the overheating and to help identify conditions at which safe and controlled operations would be ensured.

Testing involved the use of an insulated, 3-in.-diameter by 72-in.-long pipe filled with 72 in. GAC of the same type used in the overheated canister incident. The GAC-filled column was fitted with thermocouples inserted to the center line of the pipe. The thermocouples were spaced every 3.5 in. to a GAC depth of 28 in. and then every 7 in. for the remainder of the column. Thermocouples were also installed at inlet and outlet locations. Devices were provided for measuring flow rate and relative humidity. Carbon tetrachloride vapor was added to the inlet air stream by passing air over liquid carbon tetrachloride contained in a heated flask. The equipment arrangement for the bench-scale tests is shown in Figure E-1.

Figure E-1. Bench-Scale Phase I Test Equipment Schematic.

Seven bench-scale adsorption tests were conducted with inlet nominal carbon tetrachloride concentrations ranging from 1,000 ppm_v to 30,000 ppm_v. Virgin GAC was used in each test. In two of the tests, at carbon tetrachloride concentrations of 1,000 ppm_v and 5,000 ppm_v, methyl ethyl ketone (MEK) was included at 200 ppm_v. MEK is an oxidizable organic compound that may be present with carbon tetrachloride at Hanford Site liquid waste disposal sites where vapor extraction operations are planned. All tests were initiated at a superficial flow rate that corresponds to a flow rate of 500 ft³/min in the overheated canister. In the later stages of two of the tests, at carbon tetrachloride concentrations of 1,000 ppm_v and 10,000 ppm_v, the corresponding flow rates were reduced to 250 ft³/min. At the completion of each test, samples of GAC were removed from a few inches below the top of the GAC bed and pH of the water extract was determined through utilization of an industry accepted standard method. Virgin GAC was also tested in this manner.

General observations of the bench-scale testing are as follows.

- Beginning at the top of the GAC-filled column where carbon tetrachloride vapor was added, temperatures rose rapidly to a peak and then subsided at a somewhat slower rate.
- At carbon tetrachloride concentrations of 10,000 ppm_v and above, the temperature profiles exhibited well-defined peaks. At carbon tetrachloride concentrations of 5,000 ppm_v and below, the temperature profiles were irregular in shape.
- Each thermocouple in the GAC-filled column exhibited a similar response, including rising to approximately the same peak temperature for any given inlet carbon tetrachloride concentration. This created the effect of a thermal wave moving through the column as shown in Figure E-2.
- The base of the thermal waves rose and broadened with location down the column, indicating that heat was accumulating in the GAC due to the integrated temperature rise.
- At carbon tetrachloride concentrations of 10,000 ppm_v and above, a short period of near-constant temperatures on the upstream side of the thermal wave was observed as shown in Figure E-2. This stepped effect occurred at a temperature of about 92 °F in the 10,000 ppm_v test and at about 110 °F in the 20,000 ppm_v and 30,000 ppm_v tests. This may indicate that water is being desorbed from the GAC at an equilibrium temperature such that the heat generated by adsorption of carbon tetrachloride equals the heat removed by the desorption of water.
- The pH tests indicated only a small reduction in pH as a consequence of carbon tetrachloride adsorption. The pH was reduced from about 10.0 measured in the case of virgin GAC to about 9.5 measured in each of the adsorption test cases.

Figure E-2. Temperature Curves for GAC-Filled Column Bench-Scale Test at 10,000 ppm_v Carbon Tetrachloride.

E.2.4.3 Full-Scale Thermocouple Response Tests

Heated air was passed through a GAC-filled canister of the same type and size as used in the overheating incident. The objective of this testing was to determine the temperature response of three thermocouples inserted into the centerline of the canister at the 25%, 50%, and 75% depth locations. Temperature and relative humidity of the inlet and outlet airstreams were also measured.

Unheated air was first passed through the GAC-filled canister for 15 h to ensure that the GAC was in equilibrium with ambient air. No temperature effects were observed, indicating that no significant adsorption nor desorption of water vapor had occurred and that equilibrium conditions existed. Heated air at approximately 138 °F was then passed through the GAC at an average rate of 137 stdft³/min for 16 h. Observations and conclusions reached during this test include the following.

- Each of the thermocouples embedded in the GAC showed a rapid rise in temperature from about 75 °F to about 97 °F where a temperature plateau occurred. The plateau is similar to the step observed in the bench-scale tests reported earlier. The plateau temperature represents the point at which the rate of heat added by the heated air is equal to the rate of heat removal resulting from desorption of water as shown in Figure E-3.
- After the water was desorbed the temperature rose rapidly to 137 °F.
- The completion of water desorption results in a temperature wave above the 97 °F plateau that moves at a rate of 4.0 in./h.
- Calculations based on the water content of the inlet and outlet air led to the conclusion that water losses to the air corresponded to 4.8 wt% of the GAC. This compares favorably with a value of 5 wt% that is typically reported by vendors.
- The energy balance for this test is summarized as follows.
(Values reported are percent of energy added in the heated air.)

- Energy Added:	Sensible heat of heated air, 100%
- Energy Lost:	Net heat of water desorption, 75%
	Convection from canister wall, 5%
- Heat Accumulated:	GAC, 19%
	Canister metal, 1%

E.2.4.4 Thermogravimetric Analysis of GAC and Carbon Tetrachloride

The potential for chemical reactions involving GAC, with and without carbon tetrachloride, was investigated using a thermogravimetric analyzer and mass spectrometer (TGA/MS) and a differential temperature analyzer (DTA). This setup allows small samples to be heated at controlled rates while changes

Figure E-3. Thermocouple Response Test: GAC Temperature Versus Time.

in mass, changes in temperature between the sample and the heater, and composition of gases produced as the sample is heated are precisely measured. Three samples were prepared for testing: (1) a sample of virgin GAC, (2) a sample prepared by exposing virgin GAC to flowing air containing 3,000 ppm_v of carbon tetrachloride, and (3) a sample prepared by exposing virgin GAC to a flowing air stream at 60% relative humidity and 30,000 ppm_v of carbon tetrachloride for 2 h. The third sample was then tested in the TGA/MS/DTA while increasing the temperature at a rate of 5.4 °F/min to a temperature of 860 °F. Increasing the temperature in the third sample test simulated the rising temperature conditions that may have existed during the overheating incident. The TGA/MS tests were done to verify if the prepared sample would react and to define the temperatures of reaction.

The data gathered were plotted as functions of temperature and time. The heights of the curves, points of inflection, and changes in slope are indicative of the temperature at which changes in reaction rates and types of reaction occurred. Test details are presented in Appendix D.

Observations and conclusions made as a result of these tests are summarized below.

- Sample 1: Oxidation of virgin GAC began at 480 °F and became significant at 570 °F.
- Sample 2: An exothermic reaction in the GAC with adsorbed carbon tetrachloride began at 300 °F and ended at 630 °F. Oxidation of the GAC appeared to begin at a temperature of about 610 °F, which is 130 °F hotter than in the case of virgin GAC. The heat of the exothermic reaction was not measured due to the lack of a standard.
- Sample 3: A broad exothermic reaction occurred between 210 °F and 450 °F. Oxidation of the GAC appeared to begin at about 660 °F. The heat of the exothermic reaction was not measured.

E.2.4.5 Acid Formation Testing

Following the canister overheating incident, the canister was filled with water to cool the GAC. The pH of the water when removed from the canister was in the range of 0 to 1. Subsequent laboratory adsorption testing was conducted to provide insight into conditions for the formation of acids.

The test cell used in this testing consisted of a small (0.022 lb, 1.07 in³) bed of virgin GAC packed in glass tubing with quartz wool at each end and enclosed in an oven. A peristaltic pump was used to create a negative pressure and draw air and carbon tetrachloride vapor through the GAC. The concentration of the carbon tetrachloride vapor was calculated to be approximately 173,000 ppm_v (above saturation limit) with room air at 79 °F and 50% relative humidity. The flow rate achieved by the pump was 15.3 in³/min.

The loaded GAC was removed from the test cell and mixed with 100 mL of deionized water. The water/GAC slurry was stirred for 30 min and the pH was measured using an industry-accepted procedure.

Four runs of the test were made with varying initial conditions, e.g., with and without carbon tetrachloride vapor flow and with and without additional heating from the oven.

Run 1 was conducted to establish the baseline pH of the virgin GAC/water slurry. Virgin GAC was stirred in deionized water. The pH was measured at 9.93, a level attributable to the practice of rinsing the GAC with a basic solution during manufacturing.

Run 2 was conducted with 31 min of flow of carbon tetrachloride vapor through the GAC and no additional heating. The maximum GAC temperature was approximately 116 °F and the resultant GAC/water slurry pH was 10.14.

For Run 3 the oven was heated and allowed to equilibrate at 251 °F. Carbon tetrachloride vapor was then drawn through the GAC for 30 min. The final GAC temperature was 178 °F after the 30 min of carbon tetrachloride vapor flow indicating that the carbon bed was not in thermal equilibrium with the oven. The resultant pH of the GAC water extract was 9.81.

At the start of Run 4 the GAC was heated and equilibrated at various conditions to compare oven temperature versus bed temperature. The results of this heat testing are as follows:

Oven temperature	Bed temperature
302 °F	237 °F without air or vapor flow
264 °F	194 °F without air or vapor flow
392 °F	271 °F with air flow only

The GAC was then heated and equilibrated at 351 °F prior to 30 min of carbon tetrachloride vapor flow. The maximum GAC temperature reached was 378 °F after approximately 4 min of vapor flow and the final bed temperature was 360 °F. The GAC was allowed to cool and then was removed and mixed with water. The pH of the GAC extract was 2.52.

The results of the four runs indicate that a reaction occurred at some point between 178 °F and 378 °F and that it created acidic conditions in the GAC.

E.2.4.6 Potential Phosgene and Hydrochloric Acid Creation

A literature review was conducted to evaluate the potential for forming phosgene (COCl_2) and hydrochloric acid as a result of hydrolyzing or oxidizing carbon tetrachloride. This report identifies four potential reactions, their conditions and their associated heats of reaction:

- Carbon Tetrachloride Oxidation Reaction
(catalyst, $T > 338$ °F, light 2,537 Å)

- Phosgene Hydrolysis Reaction

- Carbon Tetrachloride Complete Hydrolysis Reaction
($T > 482^\circ\text{F}$)

- Carbon Tetrachloride Partial Hydrolysis Reaction
($T > 482^\circ\text{F}$ or catalyst and $T > 59^\circ\text{F}$)

The hydrochloric acid produced in these reactions may be the cause of the reduced pH observed in the quench water from the overheating incident and in the acid formation test described in the previous section. The heats of reaction at elevated temperatures were calculated and found not to vary significantly.

The report also concluded that any phosgene that was generated was likely adsorbed by the GAC and was converted to hydrochloric acid when quench water was added to the overheated canister. It is unlikely that all of the carbon tetrachloride in the canister was hydrolyzed before the overheating was observed, however, due to the limited relative mass of water present in the virgin GAC (5 wt%) and in the soil gas (60% relative humidity at 80°F). If all of the water in the GAC and soil gas were to react with carbon tetrachloride, only about 40% of the carbon tetrachloride could be hydrolyzed to hydrochloric acid.

E.3.0 MODEL DEVELOPMENT

The adsorption of carbon tetrachloride onto GAC is a combined mass and heat transfer problem operating at unsteady state. Mass and heat transfer mechanisms are likely rate limited on the microscale. Accurate three-dimensional mathematical modeling of the GAC adsorption operation, assuming uniform flow, is a complex and difficult task. The assumptions necessary to solve such a model are numerous and would not account for nonideal behavior. Extensive laboratory validation tests would likely be required.

E.3.1 PURPOSE OF MODELING

A literature survey of past modeling efforts on the combined mass and heat transfer mechanisms of GAC adsorption revealed that a set of three mass transfer partial differential equations and three heat transfer partial differential equations would need to be simultaneously solved to ensure accurate prediction of GAC temperature rise (Appendix B). In addition, several mass and heat transfer coefficients would have to be accurately estimated and assumed constant over the operating range of the adsorption process. Few process data and almost no hard data from GAC vendors exist to support the modeling.

A mass and heat transfer model, derived from basic principles, would not account for operational anomalies such as nonuniform gas flow, development of local "hot spots", chemical reactions, variable GAC particle size distribution, and other particle nonuniformities. Any of these anomalies could have contributed to the overheating incident of June 3. Hence, any model may ultimately be of limited use in predicting the occurrence of a similar incident.

A simplified model may be useful for illuminating trends and assessing the relative magnitude of effects, however. For example, it would be capable of revealing the impacts of varying superficial gas velocity or the effects of increasing the heat of adsorption. This kind of model, combined with good empirical data on the system, would be useful for developing process control parameters for the VES and adsorption systems.

E.3.2 DISCUSSION OF MECHANISMS

Interrelated mass and heat transfer mechanisms occur in the bed. These mechanisms occur simultaneously and can compete with each other during the adsorption process. Listed below are the 15 known mass and heat transfer mechanisms that occur during GAC adsorption and their probable relative importance with respect to the overheating incident.

MECHANISM	RELATIVE IMPORTANCE
1. Heat of adsorption of carbon tetrachloride	High
2. Heat of adsorption/desorption of water vapor	High
3. Convective heating of gas stream	High
4. Convective cooling of gas stream	High
5. Conductive heat transfer between particles	Low
6. Conductive heat transfer within a particle	High
7. Convective mass transfer from gas to particle	High
8. Diffusive mass transfer into pores	Low
9. Rate of adsorption of carbon tetrachloride	Low
10. Conductive heat transfer to wall (pipe or canister)	Low
11. Convective heat transfer to wall (pipe or canister)	Low
12. Convective heat transfer from wall to ambient	Low
13. Radiation heat transfer from wall to ambient	Low
14. Heat of chemical reaction (hydrolysis, oxidation)	High (if applicable)
15. Rate of chemical reaction	Low to High

The adsorption of carbon tetrachloride on GAC occurs in a mass transfer zone (MTZ) or front that slowly moves from the inlet to the outlet of the canister. This zone may be considered as a horizontal, cross-sectional slice across the vertical axis of the GAC bed. The rate of movement of this zone through the bed is related to the rate of input of carbon tetrachloride, the adsorptive capacity of the GAC, and other characteristics of the system.

The key mechanism that causes the temperature increase during normal operations is the heat of adsorption. For simple modeling purposes the heat of adsorption is assumed to be released instantaneously as the gas stream enters the MTZ. The heat of adsorption is known to vary with GAC loading capacity, temperature, and the inlet stream concentration. The relationship of heat of adsorption to these factors is developed in Section E.4.3.

Convective heating and cooling of the gas stream are also important mechanisms. Convection into the gas stream is the most effective heat transfer mechanism for removing heat from the GAC. Under normal operating conditions most other heat transfer mechanisms are relatively unimportant because they are slow or have small driving forces. The gas stream is also responsible for the convective mass transfer of carbon tetrachloride to the GAC surface, without which adsorption would not occur.

Convective heating and cooling are affected by the gas velocity. The Nusselt-type model for the convective heat transfer coefficient in turbulent flow, relating the Nusselt, Reynolds, and Prandtl numbers, shows that the convective heat transfer coefficient, h , is related to the gas velocity, v , to the 0.8 power (i.e., h is proportional to $v^{0.8}$) (Perry and Green 1984). As a result, a 50% reduction of the gas velocity will result in a 43% reduction in the convective heat transfer coefficient. For lower Reynolds numbers and flow velocities in the laminar or transition region, the power of the velocity term may drop to as low as 0.5, meaning that the change in the convective heat transfer coefficient is even less. A 50% reduction of gas velocity will reduce the convective heat transfer coefficient by 29% in these flow regimes. Hence, convective cooling of the GAC does not vary directly with flow.

As discussed in Sections E.3.3.5 and E.5.5, conductive heat transfer within a GAC particle is likely to be a limiting mechanism affecting heat dissipation. The GAC particles have an extensive interior pore structure, and the material is typically considered an insulator according GAC vendors. Heat within a GAC particle does not readily migrate to the surface of the particle. Hence, a temperature profile will develop on the particle with higher temperatures at the particle center. A discussion and analysis of this mechanism is presented in Section E.5.5.

Three other mass and heat transfer mechanisms of adsorption listed above are adsorption and desorption of water vapor, the possibility of hydrolysis and oxidative chemical reactions, and the rate of chemical reactions. All GAC has some capacity for adsorbing water. The vendor specifies an equilibrium moisture of 5% for this GAC. Moisture is readily added or removed from the GAC by an air stream flow at a given temperature and relative humidity (Appendix D). Liquid water is sometimes added to GAC to provide a heat sink to moderate temperature rise in GAC beds during the adsorption of other species. Under appropriate operating conditions this may be accomplished without the sacrifice of adsorptive capacity.

Thus, the eight mechanisms listed as important and discussed above will have the greatest influence on the behavior of the GAC adsorption system under normal operating conditions. The other seven mechanisms, while they may occur to some small extent, are not major contributors.

Recent bench-scale testing (Section E.2.4.1) has shown that the exterior paint used on the canister begins to discolor at about 550 °F (Appendix D). The gray-to-brown discoloration occurs gradually over a wide temperature range. By matching color pictures of the canister overheating incident with laboratory pictures of discolored paint coupons, it appears that much of the discolored streak on the canister reached a temperature of about 550 °F while the darkest spot probably reached a temperature of about 660 °F. The maximum temperature achieved during bench-scale adsorption testing at 30,000 ppm_v inlet carbon tetrachloride was 280 °F (Appendix D), a temperature insufficient to cause discoloration of the exterior paint.

As discussed previously, simplified modeling and bench-scale testing have shown that it is unlikely that adsorption alone could have generated enough of a temperature rise during the overheating incident to discolor the exterior paint. It is suspected that some exothermic chemical reaction occurred during the incident to raise temperatures above those expected from carbon tetrachloride adsorption alone. Possible chemical reactions may be the hydrolysis of carbon tetrachloride or oxidation of GAC and/or an unknown organic component of the soil gas.

The extremely low pH of the overheated canister quench water strongly suggests that a hydrolysis or oxidation of carbon tetrachloride occurred. A discussion of the reactions, conditions, and possibilities of converting carbon tetrachloride to phosgene and hydrochloric acid are given in Sections E.2.4.6 and E.5.0. Soil gas from wells in the area of the 216-Z-9 Trench have not been fully characterized; hence, there is the possibility of an unknown, reactive constituent, such as a ketone or aldehyde, existing in the soil gas.

E.3.3 THERMAL MODELING DEVELOPMENT

In this section key aspects of the thermal model development of the GAC adsorption system are presented and discussed qualitatively. A quantitative analysis of the model development is given in Section E.5.

An overall energy balance is first presented, followed by a deadzone (i.e., no flow) analysis. Two simple models for heat and temperature distribution are then developed and are followed by a discussion of the more complicated real case of the conduction/convection heat transfer limitation. Additional adsorption following the passage of the thermal wave is discussed. Finally, the heat and temperature rise impacts of various chemical reactions are presented.

E.3.3.1 Overall Energy Balance

The first modeling step was producing an overall energy balance on the GAC adsorption system. Both the overheating incident and the bench-scale tests were studied. In this analysis the GAC-filled canister was treated as a

"black box." That is, the adsorption dynamics occurring inside the canister were ignored and only the energy effects passing through an envelope surrounding the canister were considered.

The overall energy balance is based on the concept that the system energy accumulation equals energy input minus energy output minus losses plus energy generation. In equation form this is as follows:

$$\text{Energy (accumulation)} = \text{Energy (input - output - losses + generation)}$$

Energy input minus energy output was determined by considering stream flow rates and compositions as well as temperatures. Flow stream components, including carbon tetrachloride, water vapor, and air, were considered separately for their energy changes. Wall energy losses were estimated and deducted, as appropriate, from the totals. Lastly, energy generation due to the heat of adsorption of carbon tetrachloride and the heat of desorption of water vapor was added. The net energy accumulation calculated from the above equation was compared to the computed energy accumulation, based on before and after average temperatures of the GAC and canister wall, and the percentage difference between the values compared.

In general, there was agreement between the two energy accumulation values indicating that all the significant energy factors were included in the model. As expected, the extensive averaging of temperatures required by such an overall analysis places a premium on the accuracy and precision of thermocouple measurements, flow measurements, and VES stream component analysis. Many results were derived from very small differences between numbers. The fact that the internal canister temperature dynamics were not considered should have had no impact on the findings. A detailed, quantitative explanation and analysis of the overall energy balance is presented in Section E.5.1.

E.3.3.2 Deadzone Analysis

As was discussed earlier in this section, the maximum temperature rise measured by bench-scale testing and calculated by uniform heat distribution modeling (Section E.3.3.3) is not sufficient to explain the paint discoloration of the overheating incident. Some other contributing effect is suspected to have occurred to further raise the GAC temperature. One strong possibility is the effect of an exothermic chemical reaction such as hydrolysis of carbon tetrachloride or oxidation of GAC or other organic compounds.

Another possible explanation is the presence of a flow anomaly that caused the formation of a hot spot in the GAC. It is the purpose of the deadzone analysis to evaluate a flow anomaly such as a region of the GAC that received no VES stream flow. Such a condition might occur if an accumulation of fines blocks the gas flow path in a region of the GAC or if some large foreign object blocked flow. The resulting disruption of flow would prevent convective cooling in that zone (Boiston 1968). The presence of a deadzone would increase flow rates in nonblocked regions of the GAC. Increased flow rates would increase the loading rate as well as convective cooling and produce an uneven advance of the MTZ. No appreciable thermal effects are likely in the higher flow region. Flow anomalies other than a deadzone could occur and also generate a hot spot. A more detailed summary and analysis of these possibilities is presented in Section E.5.2.

E.3.3.3 Uniform Heat Distribution Model

An attempt was made to model, by simple means, the internal canister temperature dynamics. As was discussed before, a comprehensive model would be very complex and would involve estimation of several heat and mass transfer parameters as well as the simultaneous solution of six partial differential equations. Comprehensive modeling was not attempted. An adsorption software model, ADSORB, has been obtained, but has not yet been evaluated.

The simplest GAC temperature model possible would be a uniform distribution of heat generated by adsorption with no heat losses through the walls or heat output by convective flow of the gas stream. This adiabatic model served as the limiting case of the maximum possible uniform temperature rise due to adsorption by the GAC assuming no heat transfer. The heat generated by adsorption of carbon tetrachloride was assumed to be uniformly distributed in an MTZ and to stay in place with no transfer to adjacent GAC or the canister wall and no transfer to the passing soil gas stream. Although the model resulted in unrealistically high temperatures, it was investigated as a limiting case of adiabatic operation.

Two cases employing the uniform heat distribution model were analyzed, the overheating incident canister and bench-scale Test 7, both with a nominal 30,000 ppm_v inlet concentration. The model was analyzed assuming that an MTZ moves down the canister, leaving all of the heat of carbon tetrachloride adsorption uniformly behind as sensible heat in the GAC. The uniform heat distribution model predicted a uniform temperature of 324 °F along the length of the canister to the MTZ with a step down to the initial GAC temperature past the MTZ. For bench-scale Test 7, the uniform distribution model predicted a constant temperature of 330 °F along the length of the column to the MTZ with a step down to the initial GAC temperature past the MTZ. These temperatures are above the measured local maximum temperature of 270 °F and maximum average temperature of 112 °F of bench-scale Test 7.

E.3.3.4 Stacked Heat Distribution Model

A second simple temperature model investigated was based on a heat distribution model termed the stacked heat distribution model. In this adiabatic model all the heat of adsorption was assumed to convectively transfer downstream to the current MTZ. In this model all the heat generated during adsorption was contained in the MTZ, with no heat lost to the walls or the exiting VES stream. All GAC above and below the MTZ is at its initial temperature. In effect, all the heat generated by adsorption was stacked into the current MTZ. This model resulted in even more unrealistically high temperatures. With this model, if the MTZ were half the length of the uniform heat distribution model length, the temperature rise would be twice as great. If the MTZ were infinitesimally small in length, the temperature rise would be infinite.

Two cases of the model, the overheated canister and the bench-scale Test 7, both with a nominal 30,000 ppm_v inlet concentration, were analyzed using a 6-in.-thick MTZ. A thickness of 6 in. was arbitrarily chosen because it approximates the width of the discolored band of paint on the overheated canister. The temperature distribution for the stacked model was everywhere equal to the initial GAC temperature, except within the 6-in. width of the MTZ

in which there was a temperature spike. This spike, which occurs conceptually in the form of a rectangular thermal wave, became larger as the MTZ progressed down the canister. Because all the heat was assumed to be confined to just one MTZ, the temperature rise at the MTZ became very large: 1,200 °F for the overheating incident and 1,100 °F for bench-scale Test 7.

E.3.3.5 Conductive/Convective Model Limitations

This next step in the modeling sequence takes another step towards reality by considering conductive and convective heat transfer within the GAC canister. The previous two models assumed either no transfer as in the case of the uniform heat distribution model, or perfect, instantaneous and complete transfer of heat generated by adsorption to the MTZ in the stacked heat distribution model.

The conductive heat transfer considered was the heat conduction from the interior of a GAC particle to the outside surface of the particle. The convective heat transfer considered was the heat transfer between the outside surface of the GAC particle and the passing soil gas stream.

- These realistic mechanisms must be able to transfer heat at similar rates; otherwise, one of them becomes a rate-limiting step in the transfer. Because GAC was identified by several vendors as being a good heat insulator it was suspected that the conductive transfer may be a limiting mechanism.

This situation was analyzed by considering the Biot number, a relative comparison of convection versus conduction, for the situation of the overheating incident (Wolf 1983). The GAC particle internal and surface temperatures are not easily measurable due to the small size of the particles. Therefore, the quantitative analysis in Section E.5.5 was based on a reasonable, representative internal particle temperature. The particle surface temperature and convective heat transfer to the gas stream were calculated. The quantitative analysis and descriptive plots are given in Section E.5.5.

As a result of the quantitative analysis, it was discovered that conductive heat transfer within the GAC particle may be a significant rate-limiting mechanism that prevents the GAC from dissipating its heat rapidly. This finding agrees with the comments of GAC vendors who made a point of the characteristically slow heat dissipation from carbon beds.

E.3.3.6 Additional Adsorption Following the Thermal Wave

Another realistic feature of carbon tetrachloride adsorption that is difficult to model is additional adsorption following the thermal wave. It is likely that small amounts of carbon tetrachloride adsorption occur following the passage of the thermal wave. This additional adsorption may occur for two reasons: (1) the peak temperatures of the thermal wave inhibit complete loading and (2) diffusion of carbon tetrachloride into the smallest pores requires additional time after the wave passage.

For either case, the additional adsorption is delayed. This delay in generation of heat is evidenced by a slow rise in the temperature at the upstream base of the thermal wave.

E.3.3.7 Impact of Carbon Tetrachloride, Trace Organics, and GAC Reactions

Some thermal effect in addition to heat of adsorption is believed responsible for the overheating incident and may also have been responsible for producing the low pH measured in the quench water. Possibilities are (1) hydrolysis of carbon tetrachloride, (2) thermal decomposition of carbon tetrachloride, (3) oxidation of trace organic compounds in the extracted soil gas stream, and (4) oxidation of GAC. All these possibilities are exothermic and, under the proper conditions, will contribute to increased temperature rise.

Exothermic chemical reactions are potential generators of additional heat capable of raising the temperature of the GAC high enough to account for the canister paint discoloration. Such reactions could also initiate hydrolysis of carbon tetrachloride, which itself is exothermic. This reaction would produce hydrochloric acid and the consequent low pH of the quench water drained from the canister.

Laboratory thermogravimetric testing of the GAC as discussed in Section E.2.4.4 has shown that GAC oxidation initiates at about 480 °F, still well above temperatures achievable from heat generated by adsorption alone (Appendix D).

Trace organic compounds known to exist in the soil gas (DOE-RL 1991) at the Hanford Site include MEK, chloroform (CHCl_3), and methylene chloride (CH_2Cl_2). MEK will oxidize and generate hot spots in GAC with subsequent temperature runaway at initiation temperatures as low as 210 °F (Naujokas 1979, 1985). Other compounds identified in the literature that were very prone to reaction at low initiation temperatures were diethyl ketone, ethyl-butyl ketone, diisobutyl ketone, cyclohexanone, butyraldehyde, crotonaldehyde, propionic acid, and butyric acid (Naujokas 1985). No reaction data are given for chloroform and methylene chloride.

The initiation temperature for the hydrolysis of carbon tetrachloride adsorbed to GAC is unknown, but the reaction appears likely to have occurred during the incident as evidenced by the chloride ion content of the GAC quench water. Carbon tetrachloride may have reacted as a result of the heat generated by adsorption alone or it may have reacted after another reaction increased temperatures sufficiently to initiate hydrolysis.

Sections E.5.7, E.5.8, and E.5.9 elaborate quantitatively on the heat release and temperature rise associated with a number of the above reactions. All reactions considered in Section E.5 release more heat on a mass basis than the heat of adsorption. Thus, these reactions, to the extent and rate at which they occur, can contribute substantially to the temperature rise in the bed.

E.4.0 MODELING BASES AND ASSUMPTIONS

This section discusses the fundamental background data on carbon tetrachloride adsorption developed during this investigation and used for modeling efforts in Section E.5. The information came from a variety of sources including literature searches, application of theory, calculational methods, and bench-scale testing.

E.4.1 GAC SYSTEM PARAMETERS

Data on GAC, carbon tetrachloride, and VES operating parameters are listed with sources in Tables E-2, E-3, and E-4. This information served as a consistent database for the analysis.

Most GAC parameters were supplied by the vendor or taken from the general literature with the vendor's acknowledgement. Carbon tetrachloride data were mostly from chemical literature; the heats of adsorption were calculated from fundamental principles described in Section E.4.2. Process parameters at the time of the incident were taken from the unusual occurrence report prepared on the overheating incident. Canister parameters were from the vendor or measured during bench-scale testing.

Values of thermal conductivity and the process heat transfer coefficient represent best estimates based on the conditions of the GAC adsorption process. The heats of adsorption were calculated from fundamental data and the GAC loading was determined from bench-scale testing.

E.4.2 GAC ISOTHERM CURVES

Figure E-4 is an isothermal plot for the GAC-carbon tetrachloride system derived from vendor data. The plot presents the data in terms of GAC loading versus carbon tetrachloride concentration with parametric lines of constant temperature.

E.4.3 CALCULATION OF HEAT OF ADSORPTION

A typical vendor estimate of the heat of adsorption is 1.5 times the heat of vaporization (92 Btu/lb for CCl_4). Thus, an estimated value for the heat of adsorption of carbon tetrachloride is 138 Btu/lb. This rule-of-thumb estimation was cited by every major vendor contacted during this study. The heat of adsorption of carbon tetrachloride at various GAC loadings was calculated from fundamental isothermal data. The Clausius-Clapeyron equation, given below, was the basis for the fundamental calculation.

$$\ln(p) = -\Delta H_{ad}/RT + k \quad \text{Clausius-Clapeyron Equation}$$

where:

- p = vapor pressure (mm Hg)
- ΔH_{ad} = heat of adsorption (cal/g mol CCl_4 adsorbed)
- R = gas constant (1.98 cal/g mol $^{\circ}\text{K}$)
- T = absolute temperature, K
- k = constant

Table E-2. GAC Heat Modeling Parameters.

Parameter	Value	Source of data
Manufacturer	Envirotrol, Inc.	
Carbon Source	Coconut	Envirotrol (1993a)
Capacity (max. equil.) (lb CCl ₄ /lb GAC)	0.6/1	Envirotrol (1993a)
Specific Heat (Btu/lb °F)	0.23	Envirotrol (1993a)
Surface Area (m ² /g)	1,100 - 1,250	Envirotrol (1993a)
Bulk Density (g/cm ³)	0.44 - 0.49	Envirotrol (1993a)
Ash Content (%)	3	Envirotrol (1993a)
pH of Water Extract	9.5	Envirotrol (1993a)
Molecular Weight (g/mole)	12	Perry and Green (1984)
Bed Voidage	0.4	Estimate
Mesh Size (in.)	4 x 10 (1/16 x 3/16)	Envirotrol (1993a) Envirotrol (1993a)
Thermal Conductivity (Btu/h ft °F)	0.025	Boiz and Tuve (1976), Perry and Green (1984)
Heat Transfer Coeff. (Btu/h ft ² °F)	9.9	Boiz and Tuve (1976), Perry and Green (1984)

Table E-3. Carbon Tetrachloride Heat Modeling Parameters.

Parameter	Value	Source of data
Molecular Weight (g/mole)	153.8	Weast and Astle (1979)
Melting Point (°F)	-9.4	Weast and Astle (1979)
Boiling Point (°F)	170.2	Weast and Astle (1979)
Vapor Pressure (torr @ 77 °F)	113	Perry and Green (1984)
Water Solubility (mg/L @ 68 °F)	800	Perry and Green (1984)
Density, (liquid) (g/cm ³)	1.594	Weast and Astle (1979)
Octanol/Water Part Coeff. (unitless)	537	Not available
Henry's Law Coeff. (atm m ³ /mole @ 77 °F)	0.029	Not available
Heat of Vaporization (Btu/lb)	92	Perry and Green (1984)
Heat of Adsorption (Btu/lb)	159	Note: @ 0.20 lb CCl ₄ /lb GAC loading
	141	Note: @ 0.30 lb CCl ₄ /lb GAC loading
As calculated in this document	127	Note: @ 0.40 lb CCl ₄ /lb GAC loading

Table E-4. Process Parameters for Overheating Incident and Bench-Scale Test.

Parameter	Overheating incident value	Source of data	Bench-scale test value
VES Flow Rate (ft ³ /min)	240	WHC (1993)	500
VES Concentration (ppm _v)	28,500	WHC (1993)	1,000 to 30,000
Ambient Temperature (°F)	80	Measured	80
Relative Humidity (%)	30 to 60	Measured	50
Mass of GAC (lb)	1,760	Envirotrol (1993a)	9.04
GAC Loading (lb CCl ₄ /lb GAC)			
@ 1,000 ppm _v		Measured	0.29
@ 5,000 ppm _v		Measured	0.36
@ 10,000 ppm _v		Measured	0.42
@ 20,000 ppm _v		Measured	0.47
@ 30,000 ppm _v		Measured	0.5
Canister Bed Depth (in.)	65	Envirotrol (1993a)	72
Canister Bed Diameter (in.)	48	Envirotrol (1993a)	3
Flow Direction	Down	Envirotrol (1993a)	Down
Design Maximum Temperature (°F)	150	Envirotrol (1993a)	None
Design Maximum Flow Rate (ft ³ /min)	650	Envirotrol (1993a)	None
Design Maximum Pressure (psig)	30	Envirotrol (1993a)	None
Design Maximum Relative Humidity (%)	100	Envirotrol (1993a)	None

Figure E-4. Vendor-Supplied Isotherm Plot for Carbon Tetrachloride Adsorption on GAC.

The isothermal data were supplied by the GAC vendor in the form of a plot similar to Figure E-4. This plot related GAC loading of carbon tetrachloride to the adsorbed carbon tetrachloride partial pressure along lines of constant temperature (32 °F to 200 °F). By determining vapor pressures at fixed temperatures and loadings, calculations of the heat of adsorption according to the methods described in "Package Sorption Device System Study" (EPA 1973) were made and are listed in Table E-5. The calculated heats of adsorption bracket the rule-of-thumb estimation value.

Figure E-5 is a plot of the heat of adsorption as a function of GAC loading. The decrease in heat of adsorption with loading is typical. As loading of the GAC increases, less active adsorption sites are utilized with the result that heat of adsorption decreases. In the theoretical limiting case of carbon tetrachloride adsorbing onto a molecule of previously adsorbed carbon tetrachloride, adsorption transitions to simple condensation. In this case, the heat of adsorption is reduced to the heat of vaporization (i.e., 92 Btu/lb) (Glasstone 1946).

E.4.4 GAC LOADING VARIABILITY

Recent laboratory bench-scale testing at WSU as described in Section E.2.4.2 has produced additional fundamental data on adsorption heat and mass transfer. A small GAC adsorber was tested over a range of inlet carbon tetrachloride concentrations from 1,000 to 30,000 ppm_v. Flow into the bench-scale adsorber was held constant at a superficial velocity equivalent to 500 ft³/min in the full-scale canister. Some testing was also conducted at a velocity equivalent to 250 ft³/min to simulate flow conditions during the overheating incident.

Calculations using the bench-scale data show that GAC loading is not a constant, but a variable function of inlet concentration as expected from isotherm data. As seen in Figure E-6, a plot of GAC loading versus inlet carbon tetrachloride concentration, higher inlet carbon tetrachloride concentrations produce increased GAC loading.

Table E-5. Carbon Tetrachloride Heat of Adsorption as a Function of GAC Loading.

GAC Loading (lb CCl ₄ /lb GAC)	Heat of adsorption (Btu/lb) ΔH_{ad}
0.20	159
0.30	141
0.40	127

Figure E-5. Predicted Heat of Adsorption Versus GAC Loading.

Figure E-6. Observed GAC Loading Versus Inlet Carbon Tetrachloride Concentration.

Table E-6 relates carbon tetrachloride concentration in the gas stream, GAC loading, heat of adsorption, and the heat generated for a design production-scale operation. Note that GAC loading, which rises with carbon tetrachloride concentration, is partially offset by the falling heat of adsorption. This results in a rate of heat generation that is nearly proportional to the carbon tetrachloride concentration in the gas stream.

Additional data taken during the bench-scale testing confirm the information in Table E-6. Figure E-7 is a plot of measured GAC temperature rise in the bench-scale adsorber as a function of carbon tetrachloride concentration in the adsorption stream. This testing, which is directly scalable to the production operation, shows negligible GAC temperature rise at a concentration of 1,000 ppm_v but a temperature rise of over 200 °F for a 30,000 ppm_v concentration.

For comparison purposes, the concentration of carbon tetrachloride in a gas stream was calculated assuming that a pool of carbon tetrachloride freely vaporized into the stream at a typical ground temperature of 55 °F. Applying Dalton's Law, the calculated, equilibrium maximum gas concentration was 81,600 ppm_v. Figure E-7 was extrapolated to this maximum concentration to determine the maximum possible temperature rise generated by heat from adsorption. Figure E-8 compares the maximum estimated temperature rise with those temperature rises measured during the bench-scale testing. The maximum estimated temperature was 680 °F. This temperature is well above the initiation temperature for some of the exothermic reactions considered possible for the overheating incident. It is about the same temperature as the comparable higher darkening temperature of the canister exterior paint (660 °F).

This maximum temperature, maximum concentration analysis is only theoretical. It is very unlikely that a straight line extrapolation is appropriate in this extreme case since it is known that so many other factors change with inlet concentration. There is likely a physical bound to a maximum temperature rise according to GAC experts. This temperature bound represents a natural, physical barrier to the further adsorption of carbon tetrachloride.

Table E-6. Adsorption Parameters as a Function of Inlet Carbon Tetrachloride Concentration.

CCl ₄ Concentration (ppm _v)	Calculated GAC loading (lb CCl ₄ /lb GAC)	Heat of adsorption (Btu/lb CCl ₄)	Heat generated at 500 stdft ³ /min (Btu/h)
1,000	0.29	143	1,700
5,000	0.36	134	8,000
10,000	0.42	126	15,100
20,000	0.47	120	28,800
30,000	0.50	118	42,400

Figure E-7. Observed Bench-Scale Test GAC Temperature Rise Versus Carbon Tetrachloride Concentration.

Figure E-8. Maximum GAC Temperature as a Function of Inlet Carbon Tetrachloride Concentration.

At carbon tetrachloride concentrations of 1,000 ppm_v, the typical GAC loading based on the bench-scale testing is 0.28 lb CCl₄/lb GAC. This loading was characteristic of the operation at the 216-Z-1A Tile Field. At this loading the heat of adsorption is 144 Btu/lb CCl₄, a maximum for the range of loading experienced during operation. Calculations for production-scale operations at 1,000 ppm_v and 500 stdft³/min show that the total heat generated was 1,700 Btu/h.

As the carbon tetrachloride concentrations in the soil gas stream increase, GAC loading also increases. During the overheating incident at the 216-Z-9 Trench the measured inlet carbon tetrachloride concentration was approximately 28,500 ppm_v; hence, the GAC loading should have increased to about 0.49 lb CCl₄/lb GAC. According to Figure E-5, at this loading the heat of adsorption is reduced to about 119 Btu/lb. However, the total heat liberated is very large due to the high concentration.

Calculations for overheating incident conditions at 28,500 ppm_v and 240 stdft³/min show that the heat generated by adsorption was close to 19,000 Btu/h, over 10 times greater than for the 1,000 ppm_v case.

E.5.0 ANALYSIS AND MODELING RESULTS

This section presents the analysis and quantitative results of (1) the overall energy balance, (2) conductive and convective model heat transfer limitations, and (3) the thermal impacts of carbon tetrachloride reactions, trace organic oxidation, and GAC oxidation. Qualitative discussions of the deadzone analysis and additional adsorption following the thermal wave are presented. Lastly, the carbon tetrachloride concentration through the carbon bed was modeled and analyzed.

E.5.1 OVERALL ENERGY BALANCE

Energy balance calculations were completed for the 30,000 ppm_v carbon tetrachloride bench-scale test and for the overheated canister incident. The purpose of the energy balance was to gain insight into the importance of various mechanisms that control heat transfer within the GAC bed. A significant level of temperature, flow rate, and gas concentration data were obtained during the bench-scale test; this permitted development of a good quality energy balance. Little data existed to perform an energy balance on the overheated canister. Thus, information gained from the energy balance for the bench-scale test was used to analyze the energy balance for the overheated canister. Bench-scale test data and calculated values used in the balance are summarized in Tables E-7 and E-8. Figure E-9 shows the measured GAC center-line temperature profiles along the length of the GAC-filled column from the 30,000 ppm_v bench-scale test at six points in time where peak temperatures up to 270 °F were recorded. These peaks occurred between 3.5 and 24.5 in. from the top of the GAC.

Table E-7. Energy Balance for Bench-Scale Test at 30,000 ppm_v Carbon Tetrachloride and Overheated Canister.

	Bench-Scale Test						Overheated Canister
	15	20	32	36	44	51	112
1 Time from start of CCl ₄ , min	WSU	WSU	WSU	WSU	WSU	WSU	2-9
2 Location of test	8/17/93	8/17/93	8/17/93	8/17/93	8/17/93	8/17/93	8/17/93
3 Date of test	15:45	15:49	16:01	16:05	16:13	16:20	12:20
4 Time of day during test, h:min	476	481	476	484	492	484	240
5 Equivalent gas flow rate, calc., scfm [1]	88.9	89.8	88.9	90.3	91.9	90.4	
6 Gas velocity in 2 in. ID pipe, ft/min [2]	1.94	1.96	1.94	1.97	2.00	1.97	240
7 Gas flow rate, calc., scfm [1]	35,600	35,600	36,400	36,400	31,400	31,400	23,500
8 Inlet CCl ₄ vapor concentration, ppmv	1.65	1.67	1.69	1.71	1.50	1.48	164
9 Inlet CCl ₄ vapor flow rate, calc., lb/h	58.21	57.81	57.55	57.75	57.81	57.35	27
10 Inlet H ₂ O vapor concentration, RH%	13.75	13.76	13.76	13.76	13.76	13.76	14.34
11 Barometric pressure, psia	0.40	0.40	0.40	0.40	0.40	0.40	0.46
12 Room H ₂ O vapor saturation pressure, calc., psia [3]	5.99	6.06	5.98	6.06	6.21	6.12	977
13 Air flow rate, calc., lb/h	0.06	0.06	0.06	0.06	0.07	0.07	5.32
14 Inlet H ₂ O vapor flow rate, calc., lb/h	7.70	7.79	7.73	7.84	7.78	7.66	1146
15 Gas flow rate, calc., lb/h	33.1	33.1	33.1	11.5	11.5	11.5	681
16 Outlet CCl ₄ vapor concentration, ppmv	0.00	0.00	0.00	0.00	0.00	0.00	4.14
17 Outlet CCl ₄ vapor flow rate, calc., lb/h	43.45	43.85	51.13	55.23	63.53	67.93	27 est.
18 Outlet H ₂ O vapor concentration, RH%	0.37	0.37	0.38	0.40	0.42	0.45	0.37
19 Outlet H ₂ O vapor saturation pressure, calc., psia [3]	0.04	0.05	0.05	0.06	0.08	0.09	5.14 avg
20 Outlet H ₂ O vapor flow rate, calc., lb/h	0.124	0.124	0.124	0.124	0.124	0.124	0.124
21 CCl ₄ vapor specific heat, Btu/lb °F [3]	130	130	130	130	130	130	130
22 CCl ₄ vapor heat of adsorption, calc., Btu/lb [3] [4]	0.444	0.444	0.444	0.444	0.444	0.444	0.444
23 Water vapor specific heat, Btu/lb °F [3]	979	979	979	979	979	979	979
24 Water vapor heat of adsorption, Btu/lb [3] [5]	0.24	0.24	0.24	0.24	0.24	0.24	0.24
25 Air specific heat, Btu/lb °F [3]	72.66	72.68	73.02	73.11	73.13	73.13	85
26 Room or outdoor temperature, °F	73.94	74.01	74.52	74.57	74.46	74.52	69
27 Gas inlet temperature, °F	70.41	70.63	71.65	72.55	74.26	76.08	71 est.
28 Gas outlet temperature, °F	82.78	90.34	97.48	101.03	104.61	105.15	
29 GAC temperature at 42 in., °F	73.11	75.78	86.49	88.88	93.42	96.06	
30 Pipe surface temperature at 42 in., °F	6.42	4.33	2.84	2.80	2.35	1.76	4.10
31 Resistance, GAC to pipe, calc., h °F ft ³ /Btu	95.09	98.94	103.19	105.75	109.31	111.61	142 est.
32 Avg. temp. of GAC, calc., °F	72	95.09	98.94	103.19	105.75	109.31	59 est.
33 Previous avg. temp. of GAC, calc., °F	15	4	12	4	8	7	
34 Time between avg. GAC temps., minutes	214.22	216.39	219.04	222.62	195.44	192.25	20719
35 Heat generation rate, CCl ₄ adsorption, calc., Btu/h	19.48	18.58	9.59	3.97	-9.42	-19.94	170
36 Heat generation rate, H ₂ O adsorption, calc., Btu/h	0.00	0.00	0.00	0.00	0.00	0.00	1
37 Heat loss rate, CCl ₄ vapor, calc., Btu/h	-0.07	-0.07	-0.07	-0.05	-0.01	0.06	4
38 Heat loss rate, water vapor, calc., Btu/h	-9.38	-9.11	-7.60	-5.42	-0.55	4.25	579
39 Heat loss rate, air, calc., Btu/h	8.28	18.52	21.34	23.86	26.17	28.40	2055
40 Heat loss rate, pipe or canister, calc., Btu/h	Incremental accumulation:						
41 Generation -losses, calc., Btu	63	15	43	14	21	16	
42 From temp. rise in GAC and pipe, calc., Btu	51	29	31	19	26	17	
Cumulative accumulation:							
43 Generation -losses, calc., Btu	63	78	121	135	156	172	35 577
44 From temp. rise in GAC and pipe, calc., Btu	51	79	111	130	156	173	35 577
45 Heat imbalance, calc.	19%	-2%	8%	4%	0%	-1%	0

[1] At velocity instrument supplier standard of 70 °F and 14.7 psia

[2] Average velocity corrected by instrument internal algorithm to 70 °F and 14.7 psia

[3] ASHRAE 1989; Bowes 1971; Stull 1969; Weast 1978; Yaws 1977; Section 4 of this report

[4] Average implies an average concentration of 7,500 ppm_v and loading of 0.39 lb CCl₄/lb GAC.

[5] Below heat of vaporization of 1,050 Btu/lb at inlet temperature

Table E-8. GAC-Filled Column Bench-Scale Test at 30,000 ppm Carbon Tetrachloride: Temperature Summary for Energy Balance.

Elapsed Time (min)	16	20	32	36	44	51
Locations (a) Location Weights (b)	Temp. Weighted (°F) Temp. (c)	Temp. Weighted (°F) Temp.	Temp. Weighted (°F) Temp.	Temp. Weighted (°F) Temp.	Temp. Weighted (°F) Temp.	Temp. Weighted (°F) Temp.
T 3.5"	5.25 113.56 596.18	92.46 485.43	83.19 436.76	79.83 419.09	78.12 410.11	77.04 404.44
T 7"	3.50 230.18 805.63	179.24 627.34	96.12 336.41	90.28 315.99	85.19 298.17	82.72 289.53
T 10.5"	3.50 119.16 417.05	238.82 835.87	116.38 407.34	103.17 361.10	93.58 327.52	89.10 311.84
T 14"	3.50 110.64 387.25	110.50 386.74	239.36 837.76	172.58 604.03	110.71 387.50	99.95 349.83
T 17.5"	3.50 108.39 379.37	108.93 381.26	169.98 591.43	270.68 947.38	163.58 572.53	116.15 406.53
T 21"	3.50 106.83 373.89	108.03 378.11	106.95 374.33	110.61 387.12	258.44 904.54	208.04 728.14
T 24.5"	3.50 103.21 361.23	105.33 368.66	105.15 368.03	107.91 377.67	112.28 392.98	251.96 881.86
T 28"	5.25 100.74 528.90	103.75 544.68	104.02 546.09	107.67 565.28	107.11 562.35	107.17 562.63
T 35" (d)	7.00 70.74 495.15	69.44 486.08	76.12 532.83	78.69 550.84	105.86 741.04	106.16 743.12
T 42"	7.00 82.78 579.45	90.34 632.37	97.48 682.39	101.03 707.21	104.61 732.28	105.15 736.06
T 49"	7.00 74.77 523.38	81.43 570.00	94.21 659.46	95.90 671.30	101.59 711.12	103.06 721.45
T 56"	7.00 72.41 506.87	75.29 527.03	90.00 629.97	91.69 641.82	98.10 686.67	100.74 705.19
T 63"	7.00 71.47 500.32	72.23 505.61	83.89 587.26	86.54 605.78	92.95 650.64	96.76 677.35
T 70"	5.50 71.22 391.72	71.76 394.69	79.90 439.44	83.48 459.14	89.67 493.20	94.19 518.05
Sum of Weighted Temps.	6846.37	7123.86	7429.50	7613.75	7870.64	8036.01
Average Temp. of Column	95.09	98.94	103.19	105.75	109.31	111.61

- (a) Depth from the top of the GAC bed.
- (b) Location weights are the inches of GAC between the midpoints of thermocouple locations.
- (c) Weighted Temp. is the location temperature multiplied by the location weight.
- (d) Temperature readings at the T-35" location are uniformly skewed and therefore suspect. For purposes of this analysis, temperature data for this location are assumed to be the average of the readings for the thermocouples at the T-28" and T-42" locations, which are immediately upstream and downstream of the T-35" location, respectively.

Figure E-9. Temperature Profiles for GAC-Filled Column Bench-Scale Test at 30,000 ppm_v Carbon Tetrachloride.

Two methods were used to calculate an energy balance for the bench-scale test. In the first method, the accumulated heat was calculated from heat generation minus heat losses. This was compared to the accumulated heat calculated from the average temperature rise in the 6-ft-long column of GAC and the pipe. The total accumulated heat calculated by these two methods was equal, indicating good quality experimental data. The heat of carbon tetrachloride adsorption was selected to represent the average value appropriate for variations in loading and concentration along the length of the GAC.

In the first method for calculating the heat balance, the rate of heat accumulation in the bench-scale GAC and the 3-in. schedule 40 carbon-steel pipe was calculated by subtracting heat losses from heat generation. Heat losses considered were heat flow through the 1-in.-thick fiberglass insulation around the pipe, and those inferred from temperature and composition changes in the outlet air. Heat generation sources considered were adsorption of carbon tetrachloride and adsorption and desorption of water vapor. Chemical reactions were not evaluated as heat sources in either of the two material balances. Water vapor adsorption caused a heat gain early in the test while water vapor was being adsorbed from the inlet air. Later in the test it was being desorbed (evaporated) and resulted in a heat loss. The calculation of the pipe heat loss was adjusted so that the average heat transfer resistance was based on the difference between the center of the GAC and the pipe outside surface temperature, both measured at a point 42 in. from the top of the GAC.

The second method used for determining the rate of heat accumulation in the bench-scale test involved calculating the length-weighted average temperature rise of the GAC and the pipe during a time interval bracketing the time between peak temperatures. The time interval selected was the time from the maximum temperature indicated at one thermocouple to the time of the maximum temperature at the adjacent thermocouple. The time for the thermal wave to travel between the nominal 3.5-in. thermocouple spacings ranged from 4 to 12 min. The average rate of pipe temperature rise was assumed to be the same as the average rate of temperature rise in the GAC.

For the overheated canister, it was assumed that the total heat accumulated as calculated from the subtraction of losses from generations equaled the total heat accumulated as calculated from the temperature rise of the GAC and the surrounding canister.

Heat losses and accumulation rates are presented for both cases in Figure E-10 as a percent of heat generated by carbon tetrachloride adsorption, the heat source. The heat balance for both cases showed that less than 10% of the heat of adsorption of carbon tetrachloride was lost by all losses considered. Thus, more than 90% of the heat of adsorption remained as sensible heat in the GAC. The average heat balance calculated by the two methods is zero; i.e., the same total heat accumulated. For the short time periods evaluated in the bench-scale tests, the variance in the heat balance ranged from -41% to +55%. This broad range appears to be due to the large variation in time between peak temperatures at adjacent thermocouples. This time ranged from 4 to 12 min. Possible explanations for this apparent anomaly are (1) thermocouples are not parallel in the column and thus yield temperature data earlier or later than would otherwise be indicated by their points of insertion in the pipe wall and (2) variations in inlet flow velocity and carbon tetrachloride concentration which caused the thermal wave front velocity to vary.

Figure E-10. Contribution of Energy Balance Components Relative to Carbon Tetrachloride Heat of Adsorption.

Low outlet concentrations of water vapor and carbon tetrachloride combined with small temperature increases yielded negligible heat losses from outlet carbon tetrachloride and water vapor in both the bench-scale and the overheated canister energy balances.

E.5.2 DEADZONE ANALYSIS

During the normal operation of the activated carbon bed, substantial heat of adsorption is continually being released throughout the zone of the bed in which adsorption is occurring. This results in an increase in the temperature of the bed and in the temperature of the gas that is flowing through the bed. If the specific gas being adsorbed is present in high concentrations the temperature increase may be large and will happen rapidly. The flowing gas acts as a heat sink, and carries a substantial fraction of the heat into the downstream portion of the bed, and eventually out of the bed.

However, conditions may arise in which the flowing gas can no longer act as a sink for the heat of adsorption. If so, the carbon must act as the sole heat sink. It will heat up, and regions of abnormally high temperature, "hot spots," may form. Conditions that may lead to the formation of hot spots are listed below. These conditions resulted in the creation of hot spots in tests involving the heating of GAC loaded with readily oxidized organics (Naujokas 1979):

- Uneven bed depth due to bed movement or carbon leakage
- Stagnant bed areas, because an accumulation of fines has blocked the flow of air
- Presence of easily oxidized organics, such as ketones, aldehydes, or organic acids
- Shutdown of the bed after normal operations.

The consequences of dealing with hot spot formations depend on the conditions established in the bed. For example:

- An inert gas blanketing the bed at shutdown will exclude oxygen and prevent further heat release; the bed may then be allowed to cool by the slow dissipation of heat by conduction and convection into the atmosphere.
- A steam purge may be used to exclude oxygen, but may also desorb carbon tetrachloride. If the hot spot is too hot, this may result in the formation of carbon monoxide and hydrogen by the water-gas and water-gas shift reactions:

- The bed may be filled with liquid water that will quench all hot spots. A quantity of low pH water may then have to be dealt with if acid-producing organics were sorbed, and the carbon may be ruined for future use.
- Air may be readmitted to the bed at flows typical of normal operation. If the hot spot is not too hot (under 280 °F, approximately), the air flow will be expected to cool the bed. If it has reached temperatures of 480 °F, however, combustion of the carbon bed may result.

In most reported incidents of bed combustion in industrial plants, ketones, aldehydes, or similar materials were being adsorbed from air streams in relatively large adsorption systems (Naujokas 1979). Prior to combustion, the adsorption systems had been shutdown for extended periods of time due to mechanical failures or other circumstances, and combustion occurred when the full air stream was again introduced. These reports suggest that slow exothermic reactions occurring in a stagnant area with no air flow require the GAC to act as a heat sink. Little loss of heat by conduction occurs and eventually a small area of the carbon becomes hot enough that bed overheating or combustion of carbon results.

Using a laboratory procedure designed to exploit the conditions stated above, one researcher was able to create hot spots and bed combustion in preloaded GAC at bench-scale. The onset of combustion occurred stepwise; first, the oxidation of the organic initiated a temperature rise that in turn increased the reaction rates, then, when high enough temperatures had been reached, bed combustion initiated. Combustion could be interrupted at any point by introducing inert gas to exclude oxygen (Naujokas 1985).

E.5.3 CONDUCTIVE/CONVECTIVE MODEL LIMITATIONS

The discussion presented in Section E.3.0 on the uniform temperature distribution model and the stacked heat model showed that neither of these represents the thermal conditions with sufficient accuracy to be useful. The next step in the modeling sequence moves toward a more realistic approach by considering the conductive heat transfer limitations imposed by GAC particles.

The heat of adsorption is released when a gas molecule adsorbs on the surface of a GAC particle. Due to the extensive network of micropores within a GAC particle, carbon tetrachloride is assumed in this model to adsorb somewhat uniformly throughout the particle volume. Thus, the heat of adsorption is released throughout the volume of the particle and may uniformly heat GAC particles.

The GAC is an excellent insulator and, reportedly, has the thermal properties of cork. Hence, conductive heat transfer from the interior to the surface of a GAC particle may be expected to be a rate-limiting mechanism. As such, the temperature profile within a particle will not be uniform.

A dimensionless number, termed the Biot number ($= hd_p/k$), was calculated for this situation. The Biot number relates the rate of convective heat transfer from the particle surface to the rate of conductive heat transfer within the particle. As a general rule, values of the Biot number greater

than 0.1 indicate that internal particle resistance to heat transfer (conductivity) is significant relative to external resistance to heat transfer (convection) and is rate-limiting (Wolf 1983). The value calculated for this GAC process and materials was approximately 2. Thus, a nonuniform temperature profile may develop within a GAC particle and heat transfer by conduction from the interior of the particle may be expected to be a rate-limiting mechanism for GAC heat transfer.

Using the parameters in Tables E-2, E-3, and E-4 and assuming an arbitrary, initial particle temperature of 250 °F and a gas stream temperature of 80 °F, the temperature and heat loss curves of Figures E-11 and E-12 were calculated from a technique given in Wolf (1983). Slightly greater than 30 seconds is required for a 1/8-in.-diameter GAC particle to drop from 250 °F to a temperature of less than 85 °F at its surface, transferring essentially all of its heat to the gas stream.

While it may not seem long, 30 seconds is a significant time relative to the instantaneous heat transfer assumed in the previous models. In the 30 seconds required to cool a GAC particle from 250 °F to 85 °F, approximately 170 Btu of heat is generated within the GAC bed by 1.4 lb of carbon tetrachloride being adsorbed onto approximately 3.0 lb of GAC at process conditions similar to those during the incident. In effect, conductive heat transfer within the particle is limiting and cannot transfer heat from the interior to the surface as fast as the convective air flow is capable of removing heat.

Over time there is a heat build-up within the GAC that may or may not become significant depending on the carbon tetrachloride loading rate, concentration, and air flow velocity. This buildup may be responsible for the rise and broadening of the thermal wave profiles as seen in the bench-scale tests, shown in Figure E-2. As the thermal wave moved down the column the wave temperature profiles became slightly broader. As the peak broadened, the GAC remained at elevated temperatures for a longer period of time. This would increase the likelihood of an exothermic reaction whose initiation temperature is close to the peak temperature of the thermal wave.

Convective calculations using the data of Table E-2 show that it is quite reasonable for convective cooling processes to remove the entire heat of adsorption from the GAC. Since the events of the overheating incident indicate that this was not happening, the rate limiting conduction mechanism described above and chemical reactions may have been contributors.

E.5.4 ADDITIONAL ADSORPTION FOLLOWING THE THERMAL WAVE

When a gas containing adsorbable vapor enters a bed of fresh or newly regenerated carbon, adsorption of the vapor releases heat. The temperature at a point near the entrance to the bed rises to some maximum temperature, then subsides to the temperature of the inlet gas. If the temperature of a point midway in the GAC is plotted versus time, the temperature curve will initially be nearly flat, rise rapidly to a peak, will fall almost as rapidly, and flatten again. This is the characteristic shape of a temperature wave. As time passes the wave will move through the bed and out the exit. Because of the mass and heat transfer processes occurring in the bed, this wave always has a characteristic shape as shown in Figure E-9.

Figure E-11. Calculated GAC Particle Surface Temperature Versus Time.

Figure E-12. Calculated GAC Particle Heat Loss Versus Time.

As the adsorption starts, heat will be released due to the heat of adsorption. This will increase the temperature at that point in the bed. The increased temperature has two effects: the rate at which the adsorption occurs will be increased and the equilibrium amount that can be adsorbed on the carbon will be decreased. The bed will heat up at an increasing rate until it becomes limited by the equilibrium, at which point the temperature will start to decrease.

At the peak of the temperature wave the adsorption will essentially stop, limited by the equilibrium, and cooling will start. Cooling is principally due to convection as the flowing gas carries the heat downstream. As the bed cools, however, the equilibrium shifts to allow further adsorption of vapor as shown in Figure E-4, and the rates of the physical processes become slower. Specifically, molecular diffusion in the GAC micropores is reduced, which decreases the rate of adsorption and the most active sites are already occupied. These effects combine in such a way that the downward slope on the cooling side of the wave is less steep than the upward slope during heating. The downward slope finally approaches the initial bed temperature asymptotically, as adsorption rate and temperature driving force for heat transfer approach final equilibrium. This temperature wave gradually moves through the bed and, if continued long enough, out the outlet.

A small amount of additional carbon tetrachloride adsorption occurs following the passage of the thermal wave. Such adsorption occurs for three reasons: (1) the peak temperatures of the thermal wave prevent complete loading, (2) diffusion of carbon tetrachloride into the smallest pores requires additional time after the wave passage, and (3) the upstream GAC is loaded allowing the soil gas concentration to remain relatively high. The additional adsorption generates a small additional heat which is seen as a slow rise in overall carbon bed temperature.

These effects were seen as a slow, small overall rise in GAC bed temperature in the bench-scale adsorption tests. Such a rise in temperature counteracts GAC cooling by the gas flow and is, in part, responsible for the very slow cool down of the GAC.

E.5.5 IMPACTS OF CARBON TETRACHLORIDE REACTIONS

Carbon tetrachloride and other chlorinated organics will hydrolyze by reaction with water above the reaction initiation temperature to form chlorides, phosgene, carbon dioxide, and hydrochloric acid. When this happens the atmosphere in the adsorption vessel becomes extremely corrosive to carbon steel. The four chemical reactions presented previously in Section E.2.4.6 describe the reactants, intermediates, and products.

Temperatures may have become high enough in the MTZ of the overheated canister to initiate a hydrolysis/oxidation of the carbon tetrachloride. The evidence supporting this premise includes the extremely low pH of the quench water pumped into the canister. The pH was measured after the water had been in contact with the overheated GAC for several hours. This low pH may have resulted from the formation of hydrochloric acid in the canister by the thermal breakdown (hydrolysis) of carbon tetrachloride.

Based on pH and chemical analyses of the quench water, it was estimated that 80 lb of hydrochloric acid was generated during the overheating incident. Calculations using this quantity of product indicate that as many as 40,000 Btu may have been added to the MTZ due to the exothermic breakdown of carbon tetrachloride, based on an exothermic heat of approximately 482 Btu/lb at standard conditions (Perry and Green 1984). The rate of heat generated by adsorption alone at conditions just prior to the overheating incident was 19,000 Btu/h. Hence, the calculated heat released by hydrolysis was significant relative to heat released by adsorption. Hydrolysis reactions were probably initiated by heat buildup in the canister and may have occurred in a relatively short time frame. If the reactions occurred quickly, the resultant heat spike may have been responsible for the paint discoloration or may have been a contributor.

Bench-scale adsorption testing achieved a maximum GAC temperature of 270 °F. Samples of GAC obtained after the adsorption testing was completed and measured for pH exhibited little evidence of significant acid formation. Typically the pH was reduced from about 10.0 to about 9.5.

Analytical testing using TGA/MS/DTA under conditions that attempted to simulate the 30,000 ppm_v bench-scale test, however, revealed a broad exothermic reaction beginning at about 210 °F. This reaction was not identified nor quantified. It does provide evidence that an additional source of heat may have contributed to the temperature rise in the overheated canister.

It is also worth noting that the 28,500 ppm_v carbon tetrachloride concentration observed in the overheating incident was measured shortly after the run was initiated. In the nearly 2 h that elapsed between the 28,500 ppm_v sampling and the incident, carbon tetrachloride concentrations may have increased substantially. For perspective, the maximum possible carbon tetrachloride concentration under the Hanford Site field conditions is approximately 81,000 ppm_v. This maximum concentration was discussed in Section E.4.

Table E-9 presents heat of reaction and relative temperature rise data for several of the hydrolysis and oxidation reactions considered in this analysis.

Table E-9. Reaction Heat Release and Relative Temperature Rises.

Reactant	Reaction	Heat of reaction (Btu/lb)	Reactant quantity (lb)	Relative temperature rise ^a	Initiation temperature (°F)	Source
CCl ₄	Hydrolysis	482	0.5	x 5	>300 (?)	Appendix D
CHCl ₃	Hydrolysis	1350	0.2	x 6	Unknown	
CH ₂ Cl ₂	Oxidation	2260	0.2	x 10	Unknown	
MEK	Oxidation	14,600	0.2	x 60	>=212	Naujokas (1979)
GAC	Oxidation	14,100	1.0	x 300	>=480	Appendix D
Physical adsorption	NA	118 ^b	0.5	x 1	None	Appendix D

^aRelative temperatures rise compared to the 200 °F rise measured in bench-scale test at 30,000 ppm_v carbon tetrachloride inlet.

^bAssumed heat of adsorption.

The reactants include carbon tetrachloride, chloroform, methylene chloride, MEK, and a comparison with physical adsorption of carbon tetrachloride. The next column lists the most likely exothermic reaction to occur in GAC applications. The exothermic heat of reaction at standard conditions is listed in the third column. This column also provides the heat of adsorption of carbon tetrachloride at a loading of 0.5 lb of carbon tetrachloride per pound of GAC for comparison. The next column lists the amount of reactant per unit mass of GAC considered in the reaction heat release calculation. Values in this column for chloroform, methylene chloride, and MEK are only 40% of the value for carbon tetrachloride since these contaminants are thought to exist in the soil gas at lower concentrations than carbon tetrachloride. The next column shows the temperature rise that would be experienced by the GAC relative to the temperature rise measured for heat of adsorption alone.

As can be deduced from the table, any of the materials are capable of increasing the local GAC temperature well above that caused by adsorption of carbon tetrachloride. It would be possible for any of these compounds to generate a hot spot in the GAC capable of igniting the GAC under appropriate conditions. Ignition of GAC begins at about 480 °F in the absence of carbon tetrachloride and at about 610 °F in the presence of carbon tetrachloride. For perspective, the canister paint discoloration was determined to have occurred at about 550 °F to 660 °F. Except for carbon tetrachloride reaction, initiation temperatures for the chlorinated reactants are unknown.

The adsorption process is capable of increasing GAC temperatures approximately 200 °F at 30,000 ppm_v inlet carbon tetrachloride concentration. This rise above an ambient temperature of 80 °F would exceed the reaction initiation temperature for MEK and, thus, could create a hot spot in the GAC. An event such as this could have initiated a temperature increase that resulted in the overheating incident. A number of organic compounds besides MEK are expected to have similar low initiation temperatures (Naujokas 1985).

E.5.6 IMPACTS OF TRACE ORGANICS

The feed stream to the carbon beds may contain traces of organic compounds, in addition to the principal contaminant carbon tetrachloride (DOE-RL 1991). These compounds, too, will be adsorbed and release their heat of adsorption, just as the carbon tetrachloride does. As these organics are usually present only in trace quantities, the added heat release will usually not be a problem.

Certain organics, however, oxidize at relatively low temperatures and will liberate their heat of combustion, which is much greater than their heat of adsorption. Ketones, aldehydes, and organic acids, all oxygen-containing, are known to oxidize easily in a carbon bed (Naujokas 1979). As a measure of the effects of the combustion reaction, consider a contaminated air stream that contains 20,000 ppm_v of carbon tetrachloride and 2,000 ppm_v of MEK. The measured temperature rise due to adsorption at 20,000 ppm_v of carbon tetrachloride from the flowing stream is approximately 170 °F. If the MEK is completely oxidized, the heat of combustion is 14,600 Btu/lb and the additional calculated temperature rise will be approximately 310 °F.

Because the oxygenated organics may oxidize at relatively low temperatures, their presence increases the probability that hot spots will

form in stagnant beds. In normal operation at near-ambient temperature the oxidation may proceed so slowly that its contribution to temperature rise will not be noticed. At elevated temperatures, however, typical of operation with a highly contaminated feed air, the reaction rate may increase enough to make a significant contribution to heat release and temperature rise. The oxygenated organics also may concentrate at local spots in the GAC due to competitive adsorption with carbon tetrachloride.

As shown in Table E-9, MEK may oxidize and release large amounts of heat at temperatures achievable by carbon tetrachloride adsorption of GAC. Other ketones, aldehydes, and organic acids may have been present in the soil gas. It has been reported in the literature and discussed in Section E.3.3.2 that these compounds readily oxidize and are capable of producing "hot spots" in the GAC bed (Naujokas 1979). Comprehensive testing and analysis of the soil gas in the well associated with the overheating incident is needed to fully evaluate the possible presence of trace organics.

As a rule of thumb, ketones, aldehydes, and organic acids have relatively high heats of combustion and react at moderate temperatures. If present, and depending on the amount that reacts and the mass of GAC affected, the combustion of MEK could raise local temperatures dramatically as indicated in Table E-9. This increase in temperature could then initiate the hydrolysis of carbon tetrachloride, promote other combustion reactions, darken the exterior paint, and lead to the overheating incident experienced on June 3, 1993.

E.5.7 IMPACTS OF GAC COMBUSTION

If the carbon bed gets hot enough in operation, the bed will combust. With a flow of air through the bed of activated carbon, which provides the necessary oxygen for combustion, temperature will rise rapidly to very high levels. Melting of portions of the steel structure of adsorbers has been reported. Immediate action must be taken to stop the combustion. Temperatures at which bed ignition can occur are as low as 320 to 390 °F (Naujokas 1985).

An uncontrolled temperature rise in a GAC bed will normally follow a three-step path. First, an initial temperature rise above ambient results from adsorption of the principal contaminant (carbon tetrachloride in the soil gas). Second, if this temperature rise is great enough, the rate of oxidation of trace impurities (e.g., oxygenated organics) or other exothermic reaction may make a significant additional temperature rise. This added rise will be limited by the amount of these compounds present. Then third, if the combined temperature rise is great enough, oxidation of the GAC itself may occur. At this point the temperature may increase dramatically. Based on the temperature rise of 200 °F due to heat of adsorption at 30,000 ppm_v for the bench-scale testing, it is not likely that GAC combustion could be initiated by the heat of adsorption alone (Appendix D).

Carbon has a heat of combustion of 14,100 Btu/lb at standard conditions (Perry and Green 1984). This exothermic heat is similar to that of MEK. The effect of GAC combustion would, thus, be similar to that of trace organics in terms of its potential for raising carbon bed temperature as shown in Table E-9.

However, GAC combustion is a gas-solid reaction that generally requires more exacting conditions to initiate and maintain than the gas-gas or gas-liquid phase reactions of trace organics. GAC combustion is known to initiate over a wide range of temperatures depending on air or oxygen supply, GAC particle size, and other factors. Thermogravimetric analysis of the GAC used in the overheating incident has indicated that combustion initiates at about 480 °F (Appendix D). Reported GAC combustion temperatures range from 320 °F to well over 930 °F.

The onset of combustion can be detected by a carbon monoxide/carbon dioxide monitor in the GAC bed effluent. Significant increases in the concentrations of these gases are reason for immediate shutdown of the unit. Shutting off the source of air to the GAC bed will stop the oxidation reactions. Purging the GAC bed with nitrogen after it has been shut in will quickly stop the oxidation. The bed must then be cooled to safe operating temperatures, which can be done by allowing the passage of sufficient time or by establishing a flow of nitrogen through the bed.

E.5.8 CARBON TETRACHLORIDE CONCENTRATION THROUGH GAC BED

Having experimentally measured temperature versus location profiles for various inlet carbon tetrachloride concentrations during bench-scale testing, it was desired to back-calculate a concentration profile through the GAC. The case examined was 30,000 ppm, since this experimental case most closely represented the actual overheating incident.

The calculational procedure was straightforward. A temperature rise due to heat generated by adsorption was determined for each GAC increment between thermocouples. This figure, combined with the amount of GAC between thermocouples and its specific heat determined a total heat release which was divided by the heat of adsorption to estimate a quantity of carbon tetrachloride adsorbed on each GAC increment. This quantity was cumulatively summed through the GAC and scaled to the known inlet concentration to produce a concentration profile.

Figure E-13 is a plot of the carbon tetrachloride concentration profile. Carbon tetrachloride concentration is plotted versus canister location. A conventional "S-shape" concentration profile was calculated. Near the canister inlet, concentration was nearly constant due to the fact that this GAC had been fully loaded previously. Approaching the MTZ the concentration drops rapidly as unloaded GAC acts to remove carbon tetrachloride from the soil gas stream. After the MTZ, most of the carbon tetrachloride has been removed from the soil gas stream. There is a small, slow decline in carbon tetrachloride concentration to near zero at the outlet.

The "S-shape" of the curve is directly related to the temperature peak of the thermal wave. The details of the curve can be changed by how the temperature rise calculation is defined, however, it still retains its fundamental shape. The general shape of the curve of Figure E-13 is representative of profiles throughout a canister loading and at other inlet concentrations as well. The peak and baseline GAC temperature curves were used to define the temperature rise.

Figure E-13. Calculated Bench-Scale Test Carbon Tetrachloride Concentration in GAC Bed and Observed Temperature Profiles Versus GAC Depth.

E.6.0 CONCLUSIONS AND RECOMMENDATIONS

Listed below are the most important conclusions and recommendations of this investigation of heat modeling of GAC adsorption of carbon tetrachloride.

E.6.1 CONCLUSIONS

- Solving a mathematical model based on fundamental principles of adsorption and heat transfer is a very complex undertaking, requiring the estimation of several mass and heat transfer coefficients and the solution of several simultaneous mass and heat transfer expressions. Actual experimental data will be more effective in determining realistic limits for safe operation.
- Factors that impact the real heat and mass transfer mechanisms, but for which not enough information is currently available to attempt analytical modeling are conduction of heat through a GAC particle, conduction of heat through a GAC bed, convective heat transfer between a GAC particle and the soil gas stream, the possibility and impact of chemical reactions, the impact of unknown trace organics in the soil gas stream, the initiation temperature for exothermic reactions involving carbon tetrachloride or unknown trace organics, and the effect of flow anomalies in the GAC. More field analytical work and bench-scale testing would be required to better understand these effects.
- An overall energy balance around the canister for the overheating incident and around the column for the comparable bench-scale test gave similar results in terms of heat accumulation and heat losses by convective flow and by conduction through the canister wall. Thus, the bench-scale simulation is considered representative of the vapor extraction system employed at the Hanford Site. Approximately 90% of the heat generated by adsorption was accumulated in the system and approximately 10% was lost by various means.
- A summary of relevant temperatures obtained from the literature, bench-scale testing, and analytical testing is provided in Figure E-14. From this figure and the analyses contained in this report, it is concluded that the heat of adsorption resulting from Hanford Site operations at 28,000 ppm_v carbon tetrachloride was not sufficient to have caused discoloration of canister paint. The temperature rise resulting from the heat of adsorption at this concentration is sufficient to have initiated an exothermic reaction in the GAC, however, as indicated through laboratory testing. Identification of this reaction and its heat effects are currently unknown. The temperature rise caused by adsorption is also sufficient to have initiated oxidation of MEK, an organic compound that is occasionally found in the soil gas in conjunction with carbon tetrachloride. The heats of these reactions, added onto heat released by adsorption, may also have been sufficient to give rise to temperatures capable of initiating combustion of the GAC. The heat of the GAC reaction is clearly capable of discoloring the paint and causing other damage.

Figure E-14. Summary of Temperatures Related to Overheating Incident.

probable minimum GAC temperatures achieved in overheating incident

- Operating at a nominal carbon tetrachloride concentration of 1,000 ppm_v without additional controls poses little if any risk. A temperature rise of only a few degrees Fahrenheit is expected. Encountering MEK at 200 ppm_v in the soil gas was shown in bench-scale testing to have no measurable impact when adsorbing carbon tetrachloride at 1,000 ppm_v at a flow rate equivalent to 500 ft³/min in the full-scale vapor extraction system. Safe operations can occur without the imposition of further controls.
- Safe and controlled vapor extraction operations appear achievable at inlet carbon tetrachloride concentrations in the range of 10,000 ppt_v under certain conditions:
 1. The ambient temperatures of the GAC and the gas stream are approximately 80 °F or lower. Higher initial temperatures may dictate operating at lower carbon tetrachloride concentrations in the gas stream.
 2. The inlet gas stream is continuously monitored for concentrations of carbon tetrachloride, MEK, and other combustible organics that may be present in the soil gas.
 3. Concentration thresholds are established for these gases to prevent an unacceptable rise in temperature. The concentration of MEK capable of causing a 10 °F rise in the air temperature passing through the GAC is 70 ppm_v, for example.
 4. Means of monitoring for signs of exceeding safe design limits are provided. The use of a sensitive carbon monoxide/carbon dioxide monitor may provide an early indication of unacceptable rates of oxidation and/or hydrolysis, for example. The use of thermocouples in the GAC may provide assurance that peak temperatures created by the thermal wave are stable and in the range expected.
 5. Means of cooling GAC after a period of loading are provided. The use of nitrogen gas purge to remove oxygen and allow for long-term conductive cooling to the air or an auxiliary blower to achieve convective cooling to the air are examples.
 6. Means of suppressing an overheated condition or conditions believed to be capable of causing an overheating incident are provided. Examples include use of a nitrogen gas purge or water quenching.

E.6.2 RECOMMENDATIONS

- Additional bench-scale testing is recommended. Conditions that lead to an overheated GAC-filled canister should be tested to evaluate methods of detecting unstable conditions before overheating occurs. Testing of methods of suppressing overheated conditions will be useful for identifying an appropriate full-scale method and developing procedures for its implementation at the Hanford Site. Bench-scale testing of various gas flow rates and concentrations is also necessary for establishing safe operating thresholds when operating at elevated carbon

tetrachloride concentrations. Prewetting the GAC and/or increasing the humidity of the incoming soil gas should also be investigated as a potential technique for lowering the potential for an overheating incident.

- Extracted soil gas should be rigorously characterized before and during production operations in order to establish and maintain appropriate thresholds and conditions.
- Reaction initiation temperatures and heats for volatile organic compounds known or suspected to accompany carbon tetrachloride in the soil gas should be established through laboratory testing. This will also provide a basis for establishing appropriate operating thresholds. Current information on reactions indicates that 150 °F is an appropriate design limit.

E.7.0 REFERENCES

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ATTACHMENT E.1

A line-by-line explanation of Table E-7 will allow an understanding of assumptions inherent in the overall energy balance analysis. Calculated values are noted as "calc." in the row headings. Data from the bench-scale test and canister operation of the overheating incident are included in lines 1, 2, 3, 4, 6, 8, 10, 11, 16, 18, 26, 27, 28, 29, and 30. Values in lines 21 through 25 are from the references listed in Table A-1. Except for the velocity in line 6, the outlet carbon tetrachloride data concentration in line 16, the heat of adsorption for carbon tetrachloride in line 22, and the gas outlet temperature in line 28, the data from bench-scale Test 7 and values from reference look-up will not be discussed further.

Equivalent gas flow rate in line 5 is the velocity from line 6 times the 0.0218-ft^2 cross-section area of the 2-in.-inside-diameter pipe where the velocity probe was located times the ratio of the canister cross-section area of 12.6 ft^2 to the 3-in. pipe cross-section area of 0.0513 ft^2 .

The velocity sensor with built-in temperature correction was calibrated to read directly in linear velocity in the range of test pressures when the gas is moderately humid air. No correction or calibration was available, and no correction was made for the high concentration of a high molecular weight gas such as the carbon tetrachloride concentration of Test 7 or the 216-Z-9 Trench operation of the overheating incident. The same calibration for gas velocity was used for both the 216-Z-9 Trench and Test 7. The flow rate in standard cubic feet per minute at 70°F and 14.7 psia listed in line 7 was obtained by multiplying the velocity readings in line 6 by the 0.0218-ft^2 cross-section area of the 2-in.-inside-diameter pipe where the velocity probe was located.

The water vapor saturation pressure at room temperature, P_{ws} , of line 12 and the outlet water vapor saturation pressure, P_{ws} , of line 19 were both calculated by the following six term equation as a function of the temperatures, lines 26 and 28, respectively.

$$P_{ws}, (\text{psia}) = 2.781828^{(-10440.39708/(459.67+T) - 11.2946496 - 0.027022355(459.67+T) + 0.00001289036(459.67+T)^2 - 0.000000002478068(459.67+T)^3 + 6.5459673 \times \ln(459.67+T))}$$

The bone-dry and carbon tetrachloride-free air flow rate was calculated from Dalton's Law of partial pressure and the definition of relative humidity (RH), as measured at room temperature. The bone-dry and carbon tetrachloride free air flow rate of line 13 was calculated using the inlet carbon tetrachloride concentration from line 8, the RH from line 10, water vapor saturation pressure, P_{ws} , from line 12, the total mixed gas flow rate, V_g , from line 7, and the molar volume of $387\text{ ft}^3/\text{lb mole}$ at 70°F and 14.7 psia adjusted to the room temperature of line 26.

$$\text{Air flow rate, (lb/h)} = \frac{60 \times V_g \times (1 - \text{RH} \times P_{ws}/100 - \text{CCl}_4 \text{ ppm}_v/1000000)}{(28.96)/387}$$

Inlet water vapor flow rate of line 14 and outlet water vapor flow rate of line 20 were both calculated using the barometric pressure of line 11, the air flow rate of line 13, the relative humidities of lines 10 and 18, and the water vapor saturation pressures of lines 12 and 19. For the 216-Z-9 Trench canister, the estimated outlet relative humidity was adjusted until the ratio of outlet to inlet water vapor flow rate was equal to the average ratio of outlet to inlet water vapor flow rate for Test 7.

Feed gas mass flow rate in line 15 is the sum of carbon tetrachloride flow rate of line 9, the air flow rate of line 13, and the water vapor flow rate of line 14.

Additional comments on lines 16 through 30 are listed here. The time between inlet concentration readings and outlet concentration readings was usually too short to flush the test instrument cell volume to the room air concentration of about 0.5 ppm_v, so it was necessary to calculate the outlet carbon tetrachloride vapor concentration in line 16 from the directly measured data. A residual reading was taken, Rppm_v. The gas sample bag containing three instrument cell volumes of GAC column outlet gas was then passed through the instrument. Another reading was taken, GOppm_v. These two readings were weighted by the following equation to calculate the GAC outlet carbon tetrachloride concentration in line 16.

$$\text{GAC outlet CCl}_4 \text{ concentration, (ppm}_v\text{)} = ((4 \times \text{GOppm}_v) - \text{Rppm}_v)/3$$

The heat of carbon tetrachloride adsorption in line 22 was selected to represent the average value appropriate for the variations in concentration and loading along the length of test column and for the duration of Test 7. The average of 130 Btu/lb of carbon tetrachloride adsorbed implies an average concentration of 7,500 ppm_v and an average GAC loading of 0.164 lb CCl₄/lb GAC. During the 51 min of Test 7, it was calculated that 1.38 lb of carbon tetrachloride was loaded on 8.44 lb of GAC. The same 130 Btu/lb heat of adsorption was used for analysis of the 216-Z-9 Trench canister data where there was a similar average GAC loading of 0.2 lb CCl₄/lb GAC. During the 118 min of 216-Z-9 Trench canister use, it was calculated that 317 lb of carbon tetrachloride was loaded on 1,760 lb of GAC. Prior use of the same canister had loaded a calculated 40 lb of carbon tetrachloride for a total 357-lb load. The average concentration during generation of heat of adsorption was in the order of 15,000 ppm_v. No way of explaining this difference is suggested.

The gas outlet temperature in line 28 was measured at the relative humidity sensor in the outlet pipe less than 1 ft from the GAC column. This temperature is lower than the GAC at the outlet end of the column. The heat loss to obtain this drop in temperature is not explained. For canister analysis, the gas outlet temperature in line 28 was estimated to be above the gas inlet temperature in line 27 by the same difference as at 51 min from the start of Test 7. An outlet gas temperature was measured just below the GAC that was 12 to 25 °F higher than the GAC at the outlet end of the column. These temperature data were considered to be in error, were ignored in the analysis, and are not reported here.

At 42 in. from the top of the GAC, the temperatures listed in line 29 were measured at the center of the GAC and the temperatures listed in line 30 were measured on the outer surface of the pipe under the insulation. The

difference between these temperatures is used along with pipe surface area of 5.5 ft^2 and the heat loss from the pipe through the insulation, listed in line 40, to calculate the heat flow resistance from the center of the GAC and through the gas film inside the pipe to the pipe outer surface under the insulation as listed in line 31. The average of the resistance values from line 31, as listed in the 216-Z-9 Trench canister, was used to calculate the pipe heat loss rate in line 40 for both the pipe and the canister.

$$\text{Resistance, (h } ^\circ\text{F ft}^2\text{/Btu)} = 5.5 (T_{30}-T_{29})/\text{pipe heat loss rate}$$

The average temperatures of GAC in lines 32 and 33 for Test 7 are from Table E-8. They are at points in time when adjacent thermocouples located 3.5 in. apart in the center of the GAC were at the maximum for Test 7. The measured temperatures were given the tabulated length weights according to their positions along the height of the column. The time intervals in line 34 between maximum temperatures at adjacent thermocouples are not uniform. This may have been from variations in inlet carbon tetrachloride concentration or variations of GAC density in the column.

The average GAC temperature for the canister in line 32 is calculated by dividing the incremental heat accumulation in line 41 by the heat capacity of the GAC and the 1/4-in.-thick carbon steel of the canister surrounding it, and adding this quotient to the gas inlet temperature in line 27. The weight of GAC and steel are 1,760 and 704 lb, respectively. The specific heat of GAC and steel are 0.23 and 0.12, respectively. The canister steel weight is for the 5 ft 5-in. by 4-ft-diameter length of 1/4-in.-thick plate surrounding the GAC. Longitudinal conduction in the steel is neglected.

The heat generation rate in line 35 is the product of the difference in carbon tetrachloride flow rates, line 9 less line 17, and the carbon tetrachloride heat of adsorption in line 22.

Similarly, the heat generation rate in line 36 is the product of the difference in water vapor flow rates, line 14 less line 20, and the water vapor heat of adsorption in line 24.

The sensible heat loss rates for carbon tetrachloride vapor and water vapor in lines 37 and 38 are the product of their respective flow rates from lines 17 and 20, their respective vapor specific heats from lines 21 and 23, and the difference between gas outlet temperature in line 28 and the gas inlet temperature in line 27. A rise in temperature through the GAC is a heat loss.

The sensible heat loss rates for air in line 39 are the product of the air flow rate from line 13, the air specific heat from line 25, and the difference between gas outlet temperature in line 28 and the gas inlet temperature in line 27. A rise in temperature through the GAC is a heat loss.

The heat loss rate through the pipe or the canister in line 40 is the product of the arithmetic average surface area and temperature difference between the arithmetic average temperature of the GAC in the time interval and the room temperature divided by the average heat resistance from the GAC to the room. The surface area for the pipe, 6.68 ft^2 , is at the arithmetic average of the pipe inside diameter and the insulation outside diameter. The

surface area for the canister is 69.5 ft^2 . For Test 7, the average temperature of the GAC is the sum of the temperatures in lines 32 and 33 divided by 2. For the canister, the average temperature of the GAC was estimated and adjusted until there was agreement between the estimated temperature used in calculation of line 40 and the average temperature resulting in line 32. The average heat resistance for the insulated pipe is $8.78 \text{ h } ^\circ\text{F ft}^2/\text{Btu}$ and includes the average resistance calculated as described above. The resistance for the canister is $4.78 \text{ h } ^\circ\text{F ft}^2/\text{Btu}$ and includes the average resistance calculated above as well as the air film resistance on the outside of the canister.

The incremental and cumulative heat accumulations in lines 41 and 43 are the sum of the heat generations and losses from lines 35 through 40 multiplied by the time between average GAC temperatures in line 34.

The incremental and cumulative heat accumulations for the GAC and the pipe in lines 42 and 44 are the product of the specific heat and weight of the GAC and pipe multiplied by the difference between temperatures at the beginning and the end of the interval from lines 32 and 33. The heat capacity of the GAC is $1.904 \text{ Btu}/^\circ\text{F}$ with a weight of 8.44 lb and a specific heat of $0.23 \text{ Btu}/\text{lb } ^\circ\text{F}$. The heat capacity of the pipe is $5.46 \text{ Btu}/^\circ\text{F}$ with a weight of 45.5 lb and a specific heat of $0.12 \text{ Btu}/\text{lb } ^\circ\text{F}$.

The heat imbalance in line 45 for Test 7 and 216-Z-9 Trench operation is the difference between the cumulative heat accumulation in lines 43 and 44 as a percent of line 44. A negative value results from line 44 being greater than line 43. The total of lines 43 and 44 for the pipe are summed to the same value so the average heat imbalance is zero for the bench-scale test. For the canister, the heat accumulation in line 44 is equal to the heat accumulation rate from line 43 so the heat imbalance is zero in line 45.

APPENDIX F
POTENTIAL FOR PHOSGENE CREATION

CONTENTS

F.1.0	ANALYSIS OF POTENTIAL PHOSGENE GENERATION DURING THE CANISTER OVERHEATING INCIDENT	F-1
F.2.0	HEALTH AND SAFETY ASPECTS OF POTENTIAL PHOSGENE GENERATION	F-1
F.3.0	CARBON TETRACHLORIDE AND PHOSGENE CHEMICAL REACTIONS	F-2
F.4.0	REACTION KINETICS	F-2
F.5.0	POTENTIAL FOR GENERATING PHOSGENE	F-4
F.6.0	FATE OF POTENTIALLY GENERATED PHOSGENE	F-5
F.7.0	SUMMARY CONCLUSIONS	F-6
F.8.0	REFERENCES	F-7
F.9.0	BIBLIOGRAPHY	F-7

FIGURE:

F-1	Temperature Dependence of Carbon Tetrachloride Hydrolysis Reaction	F-4
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LIST OF ACRONYMS

CCl ₄	carbon tetrachloride
COCl ₂	phosgene
GAC	granular activated carbon
HCl	hydrochloric acid
MEK	methyl ethyl ketone
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure level
ppm _v	parts per million by volume
TWA	time-weighted average

F.1.0 ANALYSIS OF POTENTIAL PHOSGENE GENERATION DURING THE CANISTER OVERHEATING INCIDENT

This report was prepared to address the potential for generating phosgene (COCl_2) in a canister containing granular activated carbon (GAC). This canister became overheated during vapor extraction activities associated with the Carbon Tetrachloride (CCl_4) Expedited Response Action in the 200 West Area of the Hanford Site. This report addresses the following issues.

- Could phosgene have been generated during the incident? If so, what likely happened to that phosgene?
- Is the hydrolysis reaction that creates phosgene exothermic? If so, is the heat of reaction a significant factor in elevating the temperature in the canister?
- Could the GAC act as a catalyst in the system, promoting the hydrolysis reaction at a lower than normal temperature?
- How well would phosgene adsorb onto the GAC? Would it be captured in the GAC-filled canisters?
- What methods could be used for detecting phosgene adsorbed in the last two canisters in the series?
- Could phosgene react with any other compounds in the soil gas to form a ketone, such as methyl ethyl ketone (MEK) which has a low ignition temperature, and thereby contribute to the temperature increase in the canister?

The basis for addressing these issues lies in an understanding of the carbon tetrachloride and phosgene reactions that could take place in the system and the kinetic behavior associated with those reactions. It is also important to understand the significance of potential phosgene generation with regard to worker health and safety.

F.2.0 HEALTH AND SAFETY ASPECTS OF POTENTIAL PHOSGENE GENERATION

Phosgene is a very dangerous chemical that was used during World War I as a poison gas. Phosgene is a colorless gas with a suffocating odor, which when diluted with air smells like moldy hay or decaying fruit. Effects from exposure may include burns to the skin and eyes, shortness of breath, chest pain, severe pulmonary edema (accumulation of fluid in the lungs, sometimes delayed up to 24 h), and death. The Occupational Safety and Health Administration (OSHA) permissible exposure level (PEL) is set at a time-weighted average (TWA) of 0.1 ppm. The immediately-dangerous-to-life-and-health level is 2.0 ppm. The odor threshold is above the PEL (meaning that a person could be exposed to hazardous levels without being able to detect it by sense of smell) and ranges from 0.5 to 1.0 ppm. Exposure to 3 ppm results in immediate irritation of the upper respiratory tract and a brief exposure to 50 ppm can be rapidly fatal. As indicated in the following sections, it does not

- seem likely that it would have been possible to generate hazardous levels (greater than the 0.1 ppm OSHA TWA PEL) of phosgene in the exhaust to the atmosphere either during or after the overheating incident.

F.3.0 CARBON TETRACHLORIDE AND PHOSGENE CHEMICAL REACTIONS

Several carbon tetrachloride reactions are applicable to this incident. As can be seen from Equations 1 through 3 below, phosgene acts as an intermediate product in the conversion of carbon tetrachloride to carbon dioxide and hydrogen chloride. This can take place either through reaction with oxygen or through reaction with water. Equation 4 is the complete hydrolysis reaction of carbon tetrachloride. Heats of reaction are provided following each chemical equation.

- Eq. 1, Carbon Tetrachloride Oxidation Reaction
(catalyst, $T > 338^\circ\text{F}$, light 2.537 Å)

- Eq. 2, Carbon Tetrachloride Partial Hydrolysis Reaction to Phosgene Intermediate
($T > 482^\circ\text{F}$ or catalyst and $T > 59^\circ\text{F}$)

- Eq. 3, Phosgene Hydrolysis Reaction

- Eq. 4, Carbon Tetrachloride Complete Hydrolysis Reaction
($T > 482^\circ\text{F}$)

The catalysts indicated in Equations 1 and 2 above are typically heated metals, metal oxides, and metal chlorides (e.g., iron, platinum, gallium, and antimony). Hill (1960) indicates that phosgene can be generated from carbon tetrachloride at relatively low temperatures (61°F) by using ferric chloride, gallium chloride, or antimony chloride as a catalyst. Aluminum chloride and zinc chloride were demonstrated to have no effect.

F.4.0 REACTION KINETICS

Most of the references in the literature apply to dilute solutions of carbon tetrachloride in water. Only Gaisinovich and Ketov dealt with high temperature reactions in the vapor phase, and although activation energies are provided, no reaction rate constants are given. Although Hill (1960) provides both the activation energy and the reaction rate constant for the hydrolysis of carbon tetrachloride, these values are for dilute aqueous solutions rather

than for carbon tetrachloride in moist air. Also, there is some dispute in the literature as to whether the carbon tetrachloride hydrolysis reaction demonstrates first order or second order kinetic behavior. Experimenters tracking the disappearance of carbon tetrachloride in the liquid phase found the reaction to be first order, while experimenters tracking the appearance of chloride ions in the liquid phase found the reaction to be second order (Hill 1960). Gaisinovich and Ketov, who performed the vapor phase experiments, found the reaction to be second order.

Figure F-1 extrapolates from the hydrolysis kinetics of a dilute, low-temperature solution of carbon tetrachloride in water to show the temperature dependence of the first order reaction (Hill 1960). Given the differences between a low-temperature liquid phase system and a high-temperature vapor phase system, the use of the data in Figure F-1 to calculate reaction rates for the overheating incident would not be defensible. However, it does clearly show the temperature dependence of the hydrolysis reaction. The temperature curve would be roughly linear on a semi-log plot.

It is significant to note that carbon tetrachloride is very stable in water at lower temperatures. Hill (1960) identifies a half-life of about 40 years for a system at 77 °F, presumably under biologically sterile conditions. The term "half-life" means the time required for one-half of the remaining carbon tetrachloride to react with water. Approximately seven half-lives are required to consume 99% of the original carbon tetrachloride. Because of its stability carbon tetrachloride is not expected to hydrolyze appreciably at near-ambient temperatures.

Gaisinovich and Ketov, who provided activation energies for both the carbon tetrachloride and the phosgene hydrolysis reactions, state that phosgene hydrolyzes about 35 times faster than carbon tetrachloride in the vapor phase at temperatures between 570 °F and 840 °F. Consequently, the carbon tetrachloride hydrolysis reaction is the rate determining step. If there is an adequate supply of water for the hydrolysis reactions at these temperatures, then the reaction will go to completion with phosgene acting as an intermediary, forming four molecules of hydrochloric acid (HCl) for every molecule of carbon tetrachloride (Equation 4). If there is not an adequate supply of water, the reaction will continue until the available water is consumed.

To calculate a reaction rate, the following information is required: the order of the reaction (usually first or second order), the type of reactor (usually mixed or plug flow), a reaction rate constant at some temperature, and the activation energy (used to extrapolate a reaction rate constant at the desired temperature). For analysis of the overheating incident, key assumptions are activation energy from the vapor phase experiments (Gaisinovich and Ketov), second-order reaction kinetics, and a plug flow reactor. The reaction rate constant is experimentally derived, but no data were located in the literature nor through contacts with manufacturers of carbon tetrachloride. An expert consultant reported that he had conducted a similar search in April 1991 and was unable to locate a vapor phase reaction rate constant. He also concluded that kinetic studies run in water are not directly pertinent to the stability of the organic solvent in the presence of limited amounts of water. In other words, it would be unwise to try to use the low temperature, liquid phase data to model a high temperature, vapor phase reaction. Consequently, until a reaction rate constant is determined experimentally,

Figure F-1. Temperature Dependence of Carbon Tetrachloride Hydrolysis Reaction.

only qualitative conclusions regarding the behavior of carbon tetrachloride under the conditions experienced during the GAC canister overheating incident can be made.

F.5.0 POTENTIAL FOR GENERATING PHOSGENE

A number of factors lead to the conclusion that a small amount of phosgene was generated during the overheating incident.

- The localized hot spot in the carbon bed (in the region of the discolored exterior paint on the canister) may have generated the temperatures necessary to support the hydrolysis reaction. However, by the presence of the discolored paint on only one side of the canister, it does not appear that the temperature, and therefore the reaction rate, was uniform across the bed, nor throughout the mass transfer zone where carbon tetrachloride was being adsorbed when overheating was discovered.
- There is water in the soil gas to support some hydrolysis of carbon tetrachloride and phosgene. A relative humidity of 60% at 81 °F corresponds to 0.013 lb H₂O/lb dry air. If carbon tetrachloride were present at 28,500 parts per million by volume (ppm_v) as was measured during operations leading to the overheating incident, then the molar ratio of water to carbon tetrachloride in the soil gas was approximately 0.74 mole H₂O/mole carbon tetrachloride. This represents about one-third the level of water required to completely hydrolyze the carbon tetrachloride

(Equation 4) and about three-quarters the amount required to partially hydrolyze the carbon tetrachloride to a phosgene intermediate compound (Equation 3). Also, there is some moisture present in the activated carbon bed (~5% by weight) as received from the manufacturer. This is equivalent to about 0.07 mole H_2O /mole carbon tetrachloride. Since two moles of water are required for every mole of carbon tetrachloride for complete hydrolysis, it does not appear that there was adequate water available to completely hydrolyze the carbon tetrachloride.

- It is possible that a catalyst may have been present (such as iron oxides or chlorides) and may have lowered the temperature of the hydrolysis reaction. Another expert consultant contacted concerning this hypothesis, stated that it is very unlikely that the activated carbon could have acted as a catalyst for hydrolysis reactions.
- The hydrolysis reactions for carbon tetrachloride and phosgene are both exothermic and would contribute to the temperature rise in the carbon bed. The complete hydrolysis of carbon tetrachloride will release 482 Btu/lb carbon tetrachloride (41.2 kcal/gmole). For comparison, the lower heat of combustion of methane (natural gas) yields 21,571 Btu/lb. The heat release associated with the complete hydrolysis of carbon tetrachloride is therefore about 2% of that released by the combustion of methane. The heat of adsorption of carbon tetrachloride onto GAC is about 127 Btu/lb carbon tetrachloride, assuming a 40 wt% loading. Thus, the complete hydrolysis of carbon tetrachloride would yield about 280% more heat than generated by adsorption alone.

Given these factors, it is likely that some phosgene was generated during the incident. The reaction was water-limited, and the theoretical maximum possible phosgene concentration is about 20,000 ppm. This concentration is based on the assumption that all of the water in the soil gas reacts with carbon tetrachloride to form phosgene, and none of the phosgene reacts with water in the soil gas to form hydrochloric acid. This is a theoretical maximum and it is very unlikely that the phosgene concentration would be that high. Phosgene hydrolyzes much more readily than carbon tetrachloride (about 35 times faster) and would compete aggressively with carbon tetrachloride for the available water. Consequently, it is more likely that the actual phosgene concentration would be very low.

F.6.0 FATE OF POTENTIALLY GENERATED PHOSGENE

If phosgene were generated, then the conditions that supported the hydrolysis of carbon tetrachloride would also support the hydrolysis of phosgene. However, given the fact that there was only a limited amount of water available, it is possible that some of the phosgene would go unreacted (unhydrolyzed) while the soil vapor extraction system was operating. This phosgene would very readily adsorb onto the activated carbon, with a removal efficiency likely in the range of 99% in the first canister. If the phosgene

were not captured in the first canister, then it certainly would have been captured in the following two canisters in the series.

After the soil vapor extraction system was shut down, the first GAC-filled canister was flooded with water and allowed to soak for several days. Any phosgene remaining on the carbon in that canister would most certainly have hydrolyzed under those conditions to form hydrochloric acid. The fact that the rinsate had such a low pH (between 0 and 1) supports the conclusion that phosgene was formed as an intermediate in the complete hydrolysis of some of the carbon tetrachloride. An expert who was consulted on this issue stated that one of his laboratory procedures for determining the concentration of phosgene is to shake a sample with water for 4 min at room temperature to completely hydrolyze the phosgene and then measure for chloride ions. Any phosgene that was adsorbed in the last two canisters (which were not soaked with water following the overheating incident) in the series would likely have hydrolyzed by now with any moisture available in the canister. The expert consultant stated further that to measure the concentration of phosgene adsorbed on the carbon, he extracts the phosgene with a rapidly eluting solvent, such as carbon disulfide, and uses a gas chromatograph to measure the phosgene in a dark, dry, laboratory environment.

One of the issues raised was whether phosgene might react with any other compounds in the soil gas to form a ketone, such as MEK, and thereby contribute to the temperature increase in the canister through the heat of adsorption of the ketones and/or their oxidation, as they have relatively low ignition temperatures. Although phosgene could theoretically react with aromatics or saturated hydrocarbons to form ketones, it is documented that phosgene will react with ketones to form other organic compounds. Given the reactivity of phosgene with water, and the fact that there is more water in the system than there are other organics in the soil gas, it is more likely that the hydrolysis reaction would prevail over any other competing reactions. Therefore, it is unlikely that any significant concentrations of ketones were formed. The fact that the system was water-limited for the hydrolysis reactions suggests, however, that excess phosgene might have reacted with other organics that may have been in the gas stream. Until the vapor extraction system is restarted at the 216-Z-9 Trench for purposes of obtaining a representative gas sample for analysis of other organics, this possibility will remain conjectural.

F.7.0 SUMMARY CONCLUSIONS

Although it is not possible to estimate the quantities of phosgene generated from the data available, it is likely that some phosgene was generated as an intermediate product in the hydrolysis of carbon tetrachloride to form carbon dioxide and hydrogen chloride. Further, it is likely that most of the phosgene generated reacted with water to form hydrogen chloride. Any phosgene left unreacted likely adsorbed onto the activated carbon with a removal efficiency from the soil gas in the same range as demonstrated for carbon tetrachloride. Any phosgene adsorbed in the first GAC-filled canister was certainly hydrolyzed during the canister flooding. Although phosgene adsorbed in the subsequent canisters may still remain in the carbon bed, it is likely that phosgene has since hydrolyzed to form hydrogen chloride in those

canisters as well. It is unlikely that hazardous levels (greater than the 0.1 ppm OSHA TWA PEL) of phosgene occurred in the exhaust to the atmosphere either during or after the overheating incident.

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APPENDIX G

EVALUATION OF CARBON TETRACHLORIDE TREATMENT ALTERNATIVES
FOR THE CARBON TETRACHLORIDE ERA

CONTENTS

G.1.0	INTRODUCTION	G-1
G.2.0	BACKGROUND, PURPOSE, AND SCOPE	G-1
G.2.1	ERA BACKGROUND	G-2
G.2.2	PURPOSE OF EVALUATION	G-4
G.2.3	SCOPE OF EVALUATION	G-4
G.3.0	VAPOR TREATMENT DESIGN BASIS	G-5
G.4.0	CONDENSATION SYSTEMS FUNCTIONAL CRITERIA	G-7
G.5.0	EVALUATION CRITERIA	G-9
G.5.1	ARARs	G-10
G.5.2	TECHNICAL DEVELOPMENT STATUS	G-10
G.5.3	IMPLEMENTATION SCHEDULE	G-11
G.5.4	SECONDARY WASTE ISSUES	G-12
G.5.5	OPERATING AND MAINTENANCE COMPLEXITY	G-12
G.5.6	SAFETY AND RELIABILITY	G-12
G.5.7	COMPATIBILITY WITH EXISTING FACILITIES	G-13
G.5.8	CONSTRUCTION AND OPERATING COSTS	G-13
G.6.0	ALTERNATIVE CARBON TETRACHLORIDE TREATMENT SYSTEMS	G-13
G.6.1	EXISTING (BASELINE) SYSTEM	G-13
G.6.1.1	Process Description	G-13
G.6.1.2	Ability to Satisfy ARARs	G-14
G.6.1.3	Technical Development Status	G-14
G.6.1.4	Implementation Schedule	G-14
G.6.1.5	Secondary Waste Issues	G-15
G.6.1.6	Operating and Maintenance Complexity	G-15
G.6.1.7	Safety and Reliability	G-15
G.6.1.8	Compatibility with Existing Facilities	G-16
G.6.1.9	Construction and Operating Costs	G-16
G.6.2	THERMAL OXIDATION	G-16
G.6.2.1	Process Description	G-16
G.6.2.2	Ability to Satisfy ARARs	G-21
G.6.2.3	Technical Development Status	G-21
G.6.2.4	Implementation Schedule	G-22
G.6.2.5	Secondary Waste Issues	G-23
G.6.2.6	Operating and Maintenance Complexity	G-23
G.6.2.7	Safety and Reliability	G-24
G.6.2.8	Compatibility with Existing Facilities	G-24
G.6.2.9	Construction and Operating Costs	G-25
G.6.3	CONDENSATION BY MECHANICAL REFRIGERATION	G-26
G.6.3.1	Process Description	G-26
G.6.3.2	Ability to Satisfy ARARs	G-28
G.6.3.3	Technical Development Status	G-28
G.6.3.4	Implementation Schedule	G-28
G.6.3.5	Secondary Waste Issues	G-28
G.6.3.6	Operating and Maintenance Complexity	G-29
G.6.3.7	Safety and Reliability	G-29
G.6.3.8	Compatibility with Existing Facilities	G-29
G.6.3.9	Construction and Operating Costs	G-30

CONTENTS (cont.)

G.6.4	CONDENSATION BY LIQUID NITROGEN	G-30
G.6.4.1	Process Description	G-30
G.6.4.2	Ability to Satisfy ARARs	G-32
G.6.4.3	Technical Development Status	G-33
G.6.4.4	Implementation Schedule	G-33
G.6.4.5	Secondary Waste Issues	G-33
G.6.4.6	Operating and Maintenance Complexity	G-33
G.6.4.7	Safety and Reliability	G-34
G.6.4.8	Compatibility With Existing Facilities	G-34
G.6.4.9	Construction and Operating Costs	G-34
G.7.0	ALTERNATIVE TREATMENT SYSTEM COSTS	G-35
G.7.1	BASIS FOR ESTIMATED COSTS	G-35
G.7.2	RESULTS OF COST COMPARISON	G-44
G.8.0	REFERENCES	G-45

FIGURES:

G-1	Location of the 200 West Area Carbon Tetrachloride Expedited Response Action Site	G-3
G-2	Thermal Oxidation Process Flow Diagram	G-18
G-3	Dry Scrubbing Process Flow Diagram	G-20
G-4	Mechanical Refrigeration Condensation Process Flow Diagram	G-27
G-5	Liquid Nitrogen Condensation Process Flow Diagram	G-31
G-6	Estimated Cost of Carbon Tetrachloride Disposal Offsite	G-40
G-7	Estimated Cost of Carbon Tetrachloride Use at Plutonium Finishing Plant	G-41

TABLES:

G-1	Regulatory Basis and Configuration to Meet ARARs	G-11
G-2	Cost Estimate for 30,000 ppm _v Carbon Tetrachloride Concentration	G-36
G-3	Cost Estimate for 10,000 ppm _v Carbon Tetrachloride Concentration.	G-37
G-4	Cost Estimate for 1,000 ppm _v Carbon Tetrachloride Concentration.	G-38

ABBREVIATIONS, ACRONYMS, AND DEFINITIONS

ARAR	applicable or relevant and appropriate requirement
ASIL	acceptable source impact level
CCl ₄	carbon tetrachloride
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act</i>
CFR	Code of Federal Regulations
DA	dry air
DOE	U.S. Department of Energy
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ERA	expedited response action
EUAC	equivalent uniform annualized cost
GAC	granulated activated carbon
H ₂ O	water
HCl	hydrochloric acid
HEPA	high-efficiency particulate air [filter]
HX	heat exchanger
inH ₂ O	inches of water
N ₂	nitrogen
NEMA	National Electrical Manufacturer's Association
PFP	Plutonium Finishing Plant
pH	hydrogen ion activity
ppm _v	parts per million by volume
RCRA	<i>Resource Conservation and Recovery Act</i>
RETOX	Regenerative Thermal Oxidizer
stdft ³ /min	standard cubic feet per minute [at 1 atmosphere, 60°F]
THERMOX	thermal oxidation
TOE	total operating efficiency
Tri-Party Agreement	<i>Hanford Federal Facility Agreement and Consent Order</i>
trona	A natural sodium sesquicarbonate (Na ₂ CO ₃ ·NaHCO ₃ ·2H ₂ O)
VES	vapor extraction system
VOC	volatile organic compound
WHC	Westinghouse Hanford Company
wt%	weight percent

G.1.0 INTRODUCTION

This appendix reports the results of an engineering study to investigate the use of condensation to treat soil gas containing carbon tetrachloride. The carbon tetrachloride is extracted from the vadose zone in the performance of the 200 West Area Carbon Tetrachloride Expedited Response Action (ERA). The ERA utilizes a vapor extraction system (VES) that exhausts carbon tetrachloride laden vapor from the soil and directs it through canisters filled with granulated activated carbon (GAC). The GAC adsorbs 99% or more of the entering carbon tetrachloride. Clean gas vents from the GAC-filled canisters to the atmosphere. Canisters of GAC and adsorbed carbon tetrachloride are sent offsite to a commercial reactivation facility. In the reactivation process, the carbon tetrachloride is thermally destroyed. This offsite reactivation is the baseline against which the onsite treatment technology alternatives in this appendix were evaluated.

The justification for this alternative evaluation report is based on the need to determine whether there is a more cost-effective, onsite process for treating or destroying the carbon tetrachloride. The alternatives were evaluated with the assumption that the current method of using a VES to remove carbon tetrachloride from the vadose zone and adsorb it onto GAC will continue in combination with any alternative system selected. The alternative system would be located between the VES blowers and the GAC-filled canisters with the GAC providing a standby or polishing function.

The results of this report are presented in the following sections. Section G.2 introduces ERA background information and discusses the purpose and scope of this evaluation in detail. Section G.3 presents design basis information used to establish performance objectives that any alternative treatment technology would be required to meet. Section G.4 provides condensation system functional design criteria. Section G.5 describes criteria to evaluate alternatives for onsite carbon tetrachloride treatment technologies. The baseline treatment technology and three alternative technologies are identified and described in detail in Section G.6. Section G.7 compares the alternatives on the basis of cost effectiveness. Reference materials used in the evaluation are listed in Section G.8.

G.2.0 BACKGROUND, PURPOSE, AND SCOPE

In conjunction with Westinghouse Hanford Company (WHC), Ebasco Environmental performed a technical and economic evaluation of technologies capable of onsite destruction or recovery of carbon tetrachloride. The purpose of the evaluation was to identify alternative treatment technologies that might be more cost effective than the baseline technology, which is offsite GAC reactivation. To be considered acceptable, an alternative technology had to satisfy certain minimum criteria related to its ability to meet a designated set of applicable or relevant and appropriate requirements (ARARs), its technical and mechanical readiness for commercial application, and the time required for its implementation in relation to the overall ERA schedule.

This evaluation utilized criteria established specifically for the ERA and/or the Hanford Site. These criteria were extensively reported and applied in *Evaluation of Onsite Carbon Tetrachloride Treatment Alternatives for the 200 West Area* (WHC 1993). These criteria include requirements for minimal technical development and implementation time; both are required to accommodate the short, 4-year ERA project life. The criteria also include a set of ARARs based on interpretations of numerous environmental regulations.

The evaluation considered alternatives on the basis of compliance with ARARs, technical development status, implementation schedule, secondary waste issues, operating and maintenance complexity, safety and reliability, compatibility with existing facilities, and construction and operating costs. Three alternative technologies were evaluated: condensation by mechanical refrigeration and condensation by liquid nitrogen, which were evaluated in this study; and thermal oxidation, which was the lowest cost alternative evaluated in a previous study (WHC 1993). The two condensation technologies were each evaluated in three configurations (for a total of six condensation alternatives, plus thermal oxidation equals seven alternatives) that would provide various carbon tetrachloride concentrations at the inlet to polishing or standby GAC canisters. Because it was determined that recovered carbon tetrachloride may have an onsite use at the Plutonium Finishing Plant (PFP), 6 of the 7 alternatives above (2 condensation alternatives in 3 possible configurations) were also evaluated for 2 possible disposal alternatives, offsite incineration and onsite process use, for a total of 13 alternatives. In addition the baseline alternative, offsite thermal disposal during GAC reactivation, was evaluated. Annual cost estimates were produced for all 14 of these alternative configurations to evaluate the relative cost of waste disposal. These 14 alternatives were evaluated by applying 3 different carbon tetrachloride soil vapor concentrations for comparison. This makes a total of 42 cost estimates considered in Section G.7. These treatment costs were based on equivalent uniform annualized costs (EUACs) and stated in dollars per pound of carbon tetrachloride recovered or destroyed.

G.2.1 ERA BACKGROUND

In conjunction with operations from 1955 to 1973 at the Plutonium Finishing Plant (PFP), three sites in the 200 West Area of the Hanford Site were used for disposing solutions containing carbon tetrachloride. The three sites are the 216-Z-1A Tile Field, the 216-Z-9 Trench, and the 216-Z-18 Crib. Figure G-1 indicates the general location of these sites.

The *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) provides for ERAs at waste sites where early remediation will abate or significantly reduce actual or threatened degradation that might occur if action was delayed until a Remedial Investigation, a Feasibility Study, and a Record of Decision were in place. WHC has implemented the 200 West Area Carbon Tetrachloride ERA to mitigate environmental degradation associated with the existing carbon tetrachloride plume present in the vadose zone below the 200 West Area. The *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume* (DOE-RL 1991) describes in detail the background for the ERA as well as the selection of technologies that make up the existing VES. The ERA was undertaken in accordance with requirements contained in the Tri-Party Agreement (Ecology et al. 1989,

Figure G-1. Location of the 200 West Area Carbon Tetrachloride Expedited Response Action Site.

Part 3, Article XIII, Section 38) and in Title 40 of the Code of Federal Regulations (CFR) Part 300, Subpart E.

Currently, WHC operates mobile VES units to remove carbon tetrachloride from affected portions of the vadose zone in the 200 West Area. The VES units each incorporate a carbon tetrachloride treatment system consisting of canisters filled with GAC that adsorb the liberated carbon tetrachloride from the soil vapor. This baseline treatment system has proven very effective in satisfying stringent air emissions standards for volatile organic compounds (VOCs).

The existing baseline treatment system includes sending canisters of loaded GAC offsite for reactivation at vendor facilities. Reactivation destroys the carbon tetrachloride via thermal oxidation and restores the adsorptive capacity of the GAC. Canisters of reactivated GAC are returned to the Hanford Site for reuse in the VES.

The rate of soil vapor extraction has increased substantially due to carbon tetrachloride concentrations in the range from 1,000 to 30,000 ppm_v and from the use of additional and larger VES units. Based on the estimated 750 tons of carbon tetrachloride disposed to the soil and the projected extraction rate of 900 to 27,200 lb/day, the ERA should be completed in 3 to 4 years.

G.2.2 PURPOSE OF EVALUATION

The purpose of this evaluation was to identify and critically evaluate alternative carbon tetrachloride condensation technologies. The costs of waste disposal offsite and use onsite were evaluated using a wide range of soil vapor carbon tetrachloride inlet concentrations as measured during extended operation at various sites. Both of these methods meet standing process, logistical, and regulatory requirements. To utilize and integrate previous work, this study compares thermal oxidation, the lowest cost alternative from a previous evaluation (WHC 1993), with the two condensation alternatives and the baseline alternative.

The current evaluation was undertaken to address the high cost for offsite reactivation, concerns with the logistics and safety associated with transporting loaded canisters to the offsite reactivation facility in Pennsylvania, and a proposal for an onsite treatment Feasibility Study contained in the previous report (DOE-RL 1991).

G.2.3 SCOPE OF EVALUATION

The scope of the current evaluation was determined by the functional requirements of the treatment system and by the limitations of onsite facilities. These factors are described in the following paragraphs.

Performance of each alternative was made equivalent by specifying an exhaust carbon tetrachloride concentration of 10 parts per million by volume (ppm_v), the emission ARAR. Various concentrations were considered at the inlet to the polishing or standby GAC. Only well-developed, highly reliable systems concepts with many field applications of similar or the same equipment

and features were considered. This approach allowed the alternatives to be compared by cost. All of the alternative treatment systems considered in this evaluation were evaluated via comparison with each other and with the existing, baseline treatment system.

Each of the alternative treatment systems evaluated in this analysis would adsorb carbon tetrachloride and other materials from the soil vapor onto the GAC, either as the baseline treatment or as a supplementary treatment (polishing or standby). This would allow continued operation in the case of interruption of the selected alternative process. It would also serve as a backup for out of specification discharges from the selected alternative.

The potential locations for onsite treatment facilities are isolated. Any fresh water required by a treatment process would have to be trucked to the site from a remote supply site. Similarly, any wastewater produced by a treatment process would have to be trucked to a remote disposal site. Therefore, this analysis pursued dry systems in preference to wet systems when a choice was available. The primary effect of this limitation was to steer the investigation toward air-cooled condensing equipment and hydrochloric acid scrubbing systems that use dry neutralization chemicals and produce dry solid wastes. It should be noted that dry scrubbers are often selected for scrubbing hydrochloric acid in industrial applications even when water supplies and wastewater treatment facilities are readily available.

G.3.0 VAPOR TREATMENT DESIGN BASIS

A successful system for onsite carbon tetrachloride recovery or destruction must be capable of satisfying certain process and logistical parameters to ensure that carbon tetrachloride extraction and treatment under the ERA proceeds safely, effectively, and at a reasonably rapid rate. Therefore, the following parameters have been established for evaluating alternative carbon tetrachloride treatment systems:

Scheduled Operation	24 h/day, 5 day/week, 250 day/yr
Attended Operation	8 h/day
Unattended Operation	16 h/day
Operating Life Study Basis	4 years
Total Operating Efficiency	68% - the system should be available to operate at the design treatment rate 68% of the time, or about 250 day/yr (6,000 h/yr) at design capacity
Treatment System Configuration	One system at one site with vapor inlet from a VES with filters, blowers, and controls

Soil Vapor Composition	Air, carbon tetrachloride, water vapor, trace organic vapors
Soil Vapor Flow Rate	1.580 stdft ³ /min
CCl ₄ Feed Rates/Concentrations	30,000 ppm _v = 27,200 lb/day, 10,000 ppm _v = 9,070 lb/day, and 1,000 ppm _v = 907 lb/day. For the base- line, this quantity of carbon tetra- chloride would enter the treatment system just upstream of three canisters. Each canister would contain 2,000 lb of GAC and be loaded with 500 lb of carbon tetra- chloride before being removed for offsite reactivation.

For operational safety reasons, the baseline system carbon tetrachloride inlet concentration may be limited. However, for the purposes of this study, cost estimates for the entire range of soil vapor concentrations from 1,000 to 30,000 ppm_v were performed for the baseline to provide a direct comparison to the other alternatives.

Offsite CCl ₄ Treatment Cost	\$1.42/lb of GAC, including round-trip shipping. Reactivating one canister costs \$2,840.
Outlet CCl ₄ Concentration	10 ppm _v = 9 lb/day from polishing GAC
CCl ₄ Properties (from Stull 1969, Weast 1973, and Yaws 1977)	Vapor Specific Heat 0.124 Btu/lb °F at 0°F Freezing Temp. $\approx$ triple point -9 °F Heat of Fusion 7.49 Btu/lb at -9 °F Solid Specific Heat 0.201 Btu/lb °F at -9 °F Heat of Vaporization 93.8 Btu/lb at -9 °F

Dew point (°F)	Partial pressure (mmHg)	CCl ₄ Concentration (ppm _v)
19.7	22.8	30,000
-11.4	7.6	10,000
-40.4	2.28	3,000
-63.2	0.76	1,000
-103	0.076	100
-134	0.0076	10

Feed Gas Temperature/Humidity	80 °F, 60% relative humidity
CCl ₄ Human Exposure Limit	2 ppm _v for 8 h/day, 40 h/week, time-weighted average

Outdoor Air Conditions

- Ambient air temperature - -20 to 115 °F
- Relative humidity - 15% to 90%
- Rain - 0.6 in./h maximum
- Snow - 8 in./24 h, 12-in. accumulation
- Sleet and hail - less than 1% frozen precipitation; maximum diameter is 3/8 in.
- Glaze ice - about 5 day/yr
- Blowing dust and smoke - 6 mi or less visibility about 10 times/yr, 24 h each occurrence.
- Frost depth - 36 in.
- Solar radiation - minimal cloud cover year round.

G.4.0 CONDENSATION SYSTEMS FUNCTIONAL CRITERIA

The two condensation alternatives evaluated for this study are referred to as condensers, although they have a minimum temperature of -9 °F, which is below the freezing point of carbon tetrachloride. Solid carbon tetrachloride may form on the heat transfer surfaces.

The functional criteria supplied to various potential vendors are listed below and were the basis for the budgetary cost and delivery quotations received. Emissions Technology and Edwards Engineering provided conceptual design and budgetary cost quotations.

The potential suppliers were asked to provide a conceptual design, delivery estimate, and budgetary cost for a condensation system to have the following characteristics.

1. The range of soil vapor flow will be from 100 to 1,580 stdft³/min. Design inlet vapor stream is high-efficiency particulate air (HEPA) filtered and composed of 1,500 stdft³/min dry air (DA), plus 30,000 ppm_v carbon tetrachloride vapor, 20,000 ppm_v water vapor, less than 10 ppm_v of chloroform and 2-butanone, and less than 10 ppm_v total of other organic compounds, none of which is more than 1 ppm_v each. Condensing unit pressure drop shall not exceed 10 inH₂O unless an auxiliary source of pressure rise is supplied. The design inlet mass flows are 6,750 lb/h air, 1,132 lb/h carbon tetrachloride, and 87.8 lb/h water.

	ppm _v	%V	stdft ³ /min	Mol-Wt	lb/h	lb/lbDA
Air	949,300	94.93	1,500	28.96	6,750	
Water	20,700	2.07	32.7	18.02	87.8	0.013
CCl ₄	30,000	3	47.4	153.84	1,132	
Soil vapor	1,000,000	100	1,580		7,970	

2. The design operating inlet pressure of 35 inH₂O at 1,580 stdft³/min and 10 inH₂O at 250 stdft³/min will be supplied by the site operator. Inlet pressure up to 5 psig pressure relief can occur by closure of downstream valves. Design operating inlet temperature is 80 °F. Inlet temperature range is 60 °F to 110 °F. Design operating inlet humidity is 60% relative humidity, equivalent to 0.013 lb H₂O/lb DA. Inlet humidity range is 0.004 to 0.014 lb H₂O/lb DA. Inlet carbon tetrachloride concentration range is 0 to 40,000 ppm_v.
3. The condensing unit will be located between components supplied by the site operator, i.e., after the three blowers and cooler, and before the GAC-filled canisters. Three strings of three canisters in series each will be downstream of the condensing unit. Inlet connections will be from three flexible hoses of 6 in. diameter with female camlock couplings. Outlet connections will be to three flexible hoses of 6 in. diameter with female camlock couplings.
4. Three skid-mounted modules of 100 to 500 stdft³/min capacity each or one skid-mounted module of 100 to 1,580 stdft³/min capacity shall be provided. The unit(s) will be located outdoors in the 200 West Area of the Hanford Site. They will be started, run, and shut down on any day and any time of day throughout the year. The design operating life shall be 3 years, equivalent to approximately 26,000 h with 1,000 h at design inlet conditions. The design shall be able to operate continuously or intermittently without requiring scheduled replacement of components. Scheduled maintenance shall be limited to 5 h/month. Materials of construction in contact with vapor and condensed liquid shall be selected to avoid component replacement during the above life and be intact at the end of that life. Corrosion-resistant materials include fluorinated ethylene propylene and tetrafluoroethylene fluorocarbons, polyester and fiberglass, polyvinylidene fluoride, 316 L stainless steel, and carbon steel coated with Plasite 3070 (Plasite is a trademark of Wisconsin Protective Coating, Green Bay, Wisconsin), Plasite 9500, and RaiLine 201 (RaiLine is a trademark of Advanced Polymer Sciences, Inc., Avon, Ohio). Materials must be selected to resist corrosion by water and the resulting hydrochloric acid.
5. Outdoor air shall be the heat sink. No water supply shall be required for normal operation. A propylene glycol-water mixture may be used in a closed cooling loop. If required for operation of the condensing system, the condensing system supplier shall supply an air compressor, receiver, and controls to meet the approval of the site operator. Outdoor temperature, humidity, freezing mist, rain, blowing dust, and other outdoor conditions will be as noted in Section G.3.0
6. Use of a direct expansion evaporating refrigerant such as R22 or HP80 may be used in a closed-loop carbon tetrachloride condenser/freezer. Liquid nitrogen injected into the vapor stream or in a heat exchange may be used as the refrigerant. Liquid nitrogen would be supplied by the site operator.

7. Cost and conceptual design shall be provided for an outlet carbon tetrachloride concentration of 3,000 ppm_v (0.3 V%) maximum at a vapor pressure of 0.048 psia and a temperature of -40 °F, an outlet carbon tetrachloride concentration of 1,000 ppm_v (0.1 V%) maximum at a vapor pressure of 0.017 psia and a temperature of -62 °F, an outlet carbon tetrachloride concentration of 100 ppm_v (0.01 V%) maximum at a vapor pressure of 0.0016 psia and a temperature of -103 °F, and an outlet carbon tetrachloride concentration of 10 ppm_v (0.001 V%) maximum at a vapor pressure of 0.00016 psia and a temperature of -134 °F.
8. Automatic means such as recuperative heating or alternating heat cycling shall be provided to allow continuous operation with the specified inlet conditions, an outlet temperature between 35 °F and 80 °F, and an outlet humidity not higher than 0.013 lb H₂O/lb DA. Defrost of heat exchange surfaces may be by electrical power, hot refrigerant gas defrost, valve switching of coils from refrigerant evaporation to refrigerant condensation, valve switching of warm brine and cold brine to coils, or other site operator-approved means that avoid reentrainment of the carbon tetrachloride vapors.
9. Electrical power will be provided by the site operator at 460 V 3-phase. The supplier shall state connected and operating loads.
10. Control and instrumentation shall be provided with 115 V 1-phase power through a transformer supplied with the system. All control and instrumentation readout and adjustment shall be located in a National Electrical Manufacturer's Association (NEMA) type 4 cabinet with a light and a weatherproof outlet. Monitoring and control signals shall be available to and be compatible with the site operator's monitor and control system.
11. A condensate collection, storage, and delivery system will be based on a maximum collection rate of 2,300 gal/day. It will be mounted on a separate skid, provide a 5,000-gal storage tank, and a means such as a pump to fill and empty it of collected carbon tetrachloride, water, and any other trace compounds. The pump shall empty the tank into a 4,000-gal, 53,000-lb load-weight tank truck in not over 2 h at a flow rate of not less than 40 gal/min. The tank shall vent to the VES blower suction so the vapors can be recondensed. The tank shall have a level switch and indication of low, high, and high-high and a vent connection to the blower inlet on the blower trailer. A back pressure regulator shall be provided to control tank negative pressure.

G.5.0 EVALUATION CRITERIA

This section describes criteria developed in this analysis to evaluate alternatives for on-site carbon tetrachloride treatment technologies. Sections G.5.1, G.5.2, and G.5.3 discuss the following three criteria:
(1) ARARs based on the carbon tetrachloride concentration of the clean

discharge air, (2) technical development status, and (3) implementation schedule, respectively.

Five lesser criteria were developed to assess and compare the relative strengths and weaknesses of each alternative with each other and with the baseline treatment system. These five, as described in Sections G.5.4 through G.5.8, include secondary waste issues, operating and maintenance complexity, safety and reliability, compatibility with existing 200 West Area facilities, and construction and operating costs.

G.5.1 ARARs

The ARARs used in the *Evaluation of Onsite Carbon Tetrachloride Treatment Alternatives for the 200 West Area ERA* (WHC 1993) to evaluate the acceptability of alternative treatment technology were based largely on those developed for evaluating onsite treatment alternatives in the *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume* (DCE-RL 1991). Those ARARs were developed very conservatively and on the basis that, even though the ERA is an interim CERCLA action and is exempted from permitting, any final action required under an eventual Record of Decision would not necessarily be exempted. They included ARARs for operations, such as well boring, that are not relevant to this evaluation of carbon tetrachloride condensation system alternatives.

For the current evaluation, a carbon tetrachloride concentration of 10 ppm_v in clean vapor exhausted to the atmosphere represents the emission ARAR to encompass all requirements for carbon tetrachloride as summarized in Table G-1. A three-stage GAC system for baseline adsorption or polishing will meet this limit with 99% carbon tetrachloride removal at 1,000 ppm_v inlet concentration and a 99.97% removal at 30,000 ppm_v inlet concentration. The thermal oxidation alternative has additional ARARs pertaining to hydrochloric acid emissions that were analyzed and reported in WHC (1993) and summarized in Table G-1.

These requirements are satisfied by all alternatives identified in this evaluation. Again, the current compliance would continue.

G.5.2 TECHNICAL DEVELOPMENT STATUS

To be considered for replacing the baseline treatment system, alternatives must incorporate technologies that do not require any significant degree of further development. At best, the development program might not be successful. At worst, an extensive development program conducted to generate or optimize design parameters specific to the ERA could consume a significant portion of the 3 to 4 years projected for ERA operation.

Table G-1. Regulatory Basis and Configuration to Meet ARARs.

ARARs	Regulation	Requirements	Configuration to meet regulation
Radiation protection air emissions and radionuclide emissions from DCE facilities	Chapter 246-247 WAC and NESHAPS 40 CFR Part 61, Subpart H	BARCT 0.1 mrem/yr dose equivalent to public	HEPA filters and online emission monitoring
Prevention of significant deterioration	Chapter 173-403-080 WAC and 40 CFR Section 52.21	BACT to limit CCl ₄ emissions to less than 40 ton/yr	Three-stage GAC polishing
New sources of toxic air pollutants	Chapter 173-460 WAC	T-BACT to meet ASIL of 0.067 µg/m ³ maximum annual average for CCl ₄ and 23.3 µg/m ³ h 24-h average for HCl	Three-stage GAC polishing
Process vents and equipment leaks	RCRA Part 264, TSD, Subparts AA, BB and X	Total organic emissions less than 3 lb/h or 95% less than inlet	Three-stage GAC polishing and closed-loop purge of sampling
Incinerator standards (thermal oxidation only)	Chapter 173-303-670 WAC and RCRA Part 264, Subpart O	HCl emissions less than 4 lb/day	Emission scrubber
Hazardous substance release reporting	40 CFR Part 302	CCl ₄ emissions less than 10 lb/day, HCl less than 5,000 lb/day, ²²⁰ Rn or ²²² Rn less than 0.1 Ci, ²¹⁰ Pb less than 0.01 Ci	Three-stage GAC polishing to 10 ppm, for 93 lb/day at 1,500 stdft ³ /min

ARAR	Applicable or Relevant and Appropriate Requirements
ASIL	Acceptable Source Impact Level
BACT	Best Available Control Technology
BARCT	Best Available Radionuclide Control Technology
CFR	Code of Federal Regulations
CCl ₄	carbon tetrachloride
HCl	hydrochloric acid
NESHAPS	National Emission Standards for Hazardous Airborne Pollutants
RCRA	Resource/Conservation and Recovery Act
T-BACT	Best Available Control Technology for Toxics
TSD	Treatment, Storage, and Disposal
WAC	Washington Administrative Code

G.5.3 IMPLEMENTATION SCHEDULE

The ERA is already in progress, and the baseline, offsite carbon tetrachloride treatment system is already implemented. The rate of soil vapor extraction has increased substantially due to carbon tetrachloride concentrations in the range from 1,000 to 30,000 ppm_v and from the deployment of additional and larger VESs. Based on the estimated 50% extraction of the 750 tons of carbon tetrachloride disposed to the soil, and the projected extraction rate of 900 to 27,200 lb/day, the ERA will be completed in 3 to 4 years.

The equipment and installation costs for an alternative system would be amortized over the anticipated ERA operating period of 3 to 4 years rather than the 10 to 30 years common to industrial projects. Thus, in terms of economics and the resulting carbon tetrachloride treatment cost, it is imperative that any alternative treatment system be capable of rapid deployment. For purposes of this analysis, it was determined that one year would be an acceptable, maximum deployment time. The projected implementation schedule for an alternative treatment system should not exceed 1 year for engineering,

fabrication, installation, and commissioning. This would result in an operating system by the end of fiscal year 1994.

G.5.4 SECONDARY WASTE ISSUES

The types and quantities of secondary wastes produced are of concern with any technology deployed to support the environmental restoration mission at the Hanford Site. For processes that meet the primary criteria for consideration as alternatives to the baseline carbon tetrachloride treatment system, secondary waste issues can be used as a secondary criterion to assess the process and compare it with others.

As a minimum, it would be necessary that a means exist to dispose the secondary waste(s) efficiently. This efficiency would include cost as well as logistics. Other secondary waste issues of importance would include items such as classification, handling characteristics, and total volume.

G.5.5 OPERATING AND MAINTENANCE COMPLEXITY

The basis for this analysis assumed that any alternative treatment system would be required to operate 16 of 24 h/day without routine operator attention. The basis also assumed that routine maintenance would be performed during the two days per week when the system was not operating. These requirements favor intrinsically simple processes that rely heavily on scheduled, preventive maintenance for reliability. Processes that are complex to operate would require intricate monitoring and control systems to support unattended operation. Similarly, processes that incorporate a large number of equipment components subject to failure or components requiring specialized maintenance skills would not allow maintenance during short shut downs.

G.5.6 SAFETY AND RELIABILITY

Any alternative treatment system would have to offer a high level of safety to prevent injury to operating and maintenance personnel, the public, the environment, and the treatment system equipment. Preferably, the safety would be intrinsic to the equipment design and operating procedures rather than dependent on monitoring and control systems. A typical intrinsic design feature is an exhaust stack of adequate height and adequately high discharge velocity. These stack features would assure safety from toxic emissions for nearby uninvolved individuals.

In terms of reliability, the basis for this analysis assumed that an alternative treatment system would operate safely and reliably 24 h/day and 5 days week. Additionally, for 16 of the 24 operating hours per day, an operator would not normally be present to attend the operation. These requirements are not particularly stringent by industrial standards. However, each alternative treatment system was assessed to determine the probability that it could satisfy these requirements.

G.5.7 COMPATIBILITY WITH EXISTING FACILITIES

Any alternative treatment system would have to be compatible, to some degree, with existing Hanford Site facilities. For example, the projected power consumption for the alternative system could not exceed the power supply available to the proposed treatment site. As another example, since there is no existing process water supply to the proposed treatment sites, alternative systems that require makeup water are not attractive.

G.5.8 CONSTRUCTION AND OPERATING COSTS

Cost was an important factor in evaluating alternatives to the baseline treatment system. Factors in the design basis for this analysis determined that the treatment cost for the baseline system is \$5.68/lb of carbon tetrachloride treated. Subsequently, treatment costs were estimated for each alternative based on EUAC divided by the total pounds of carbon tetrachloride treated each year. These costs are reported in Section G.7 in dollars per pound of carbon tetrachloride treated. Alternatives that indicated a significant savings compared with the baseline treatment cost were attractive.

G.6.0 ALTERNATIVE CARBON TETRACHLORIDE TREATMENT SYSTEMS

This analysis identified a group of technologies or systems as potential alternatives to the baseline, offsite carbon tetrachloride treatment system. Section G.6.1 describes the baseline treatment system and provides an assessment of its attributes in terms of its ability to satisfy ARARs, technical development status, implementation schedule, secondary waste issues, operating and maintenance complexity, safety and reliability, compatibility with existing facilities, and construction and operating costs. Sections G.6.2 through G.6.4 describe three treatment system technologies (thermal oxidation, condensation by mechanical refrigeration, and condensation by liquid nitrogen) in terms of these same attributes.

G.6.1 EXISTING (BASELINE) SYSTEM

In the existing baseline treatment system, canisters containing GAC loaded with adsorbed carbon tetrachloride are removed from VES service and replaced with canisters of reactivated GAC. The loaded canisters are shipped to an offsite vendor facility where carbon tetrachloride is treated by thermal destruction. The vendor returns canisters of reactivated GAC to the Hanford Site. The following sections describe attributes of the baseline treatment system in detail.

G.6.1.1 Process Description

After a GAC-filled canister is loaded with carbon tetrachloride (i.e., after it has reached its design adsorption capacity), VES operators shut down the VES and manually close inlet and discharge valves to isolate the canister. Next, the operators disconnect and remove the loaded canister and replace it

with the secondary canister in the treatment train. Thus, the secondary canister becomes the primary, the tertiary canister becomes the secondary, and a canister containing reactivated GAC is placed in tertiary position. Finally, the loaded canister is transferred to a staging area to await loading and shipment to Pennsylvania for reactivation.

According to the terms of an existing contract, Envirotrol personnel collect loaded canisters and transport them by truck to the Envirotrol reactivation facility located in Pennsylvania. At the Pennsylvania facility, Envirotrol personnel transfer carbon tetrachloride-laden GAC from the loaded canisters into a high-temperature thermal processor. The processor is designed and operated to convert carbon tetrachloride to carbon dioxide and hydrochloric acid at high efficiencies. A scrubber contacts processor flue gas with an aqueous solution of sodium hydroxide. The scrubbing captures particulates formed by attrition of the GAC during its passage through the processor and also neutralizes hydrochloric acid and carbon dioxide produced by oxidation of the carbon tetrachloride. Clean exhaust gas vents from the scrubber to the atmosphere.

Under the offsite treatment contract, Envirotrol is responsible for supplying the ERA with fresh GAC-filled canisters. In Pennsylvania, Envirotrol personnel decontaminate the empty canisters, refill them with fresh and reactivated GAC, and transport them by truck back to the Hanford Site.

G.6.1.2 Ability to Satisfy ARARs

The baseline treatment system satisfies all ARARs established for this evaluation. No carbon tetrachloride is released from the loaded canisters prior to their arrival at the Envirotrol treatment facility in Pennsylvania. Similarly, none of the carbon tetrachloride is destroyed or otherwise converted at the Hanford Site to produce hazardous or nonhazardous byproducts.

Envirotrol's treatment facility in Pennsylvania is permitted under the *Resource Conservation and Recovery Act* (RCRA) regulations for receipt, storage, and treatment of hazardous wastes. Flue gas discharged by the Envirotrol incinerator is regulated by a Pennsylvania air quality permit. The incinerator is equipped with a flue gas scrubber that captures particulates and neutralizes hydrochloric acid by contacting the flue gas with an aqueous sodium hydroxide solution to clean the gas before it vents to the atmosphere.

G.6.1.3 Technical Development Status

The carbon tetrachloride incineration and the hydrochloric acid neutralization steps included in the baseline treatment system are based on fully developed technologies. Both high-temperature incineration of halogenated VOCs and liquid caustic scrubbing of flue gas have been used successfully in industrial applications for decades.

G.6.1.4 Implementation Schedule

The baseline treatment system is already implemented at the Hanford Site. Specifically, WHC has developed the staging area required for storing

and shipping loaded canisters; developed the staging area required for receiving and storing fresh canisters; purchased the necessary equipment and trained VES operators to transfer canisters at the site; purchased or ordered a sufficient number of canisters to provide for inventories of loaded canisters, fresh canisters, and canisters absent from the site for treatment; and executed a contract with Envirotrol that provides for offsite GAC reactivation and carbon tetrachloride treatment.

G.6.1.5 Secondary Waste Issues

In the baseline treatment system, the loaded canisters are considered to be hazardous secondary waste. Canisters of GAC represent the only onsite secondary waste from this process. At Envirotrol in Pennsylvania, secondary waste is produced during the reactivation process. Hydrochloric acid results from carbon tetrachloride destruction and particulates result from GAC attrition. Scrubbing of the incinerator flue gas with aqueous sodium hydroxide produces secondary waste. The resultant secondary waste is activated carbon sludge and sodium chloride. Handling and disposing those secondary wastes are Envirotrol's responsibility under the treatment contract. The cost of handling and disposing are included in the contracted price for GAC reactivation.

G.6.1.6 Operating and Maintenance Complexity

The baseline treatment system has proven to be simple to operate. The operating functions required of personnel at the Hanford Site consist of routine canister connection, disconnection, and transfer. Envirotrol personnel have responsibility for all canister maintenance under terms of the existing reactivation contract.

G.6.1.7 Safety and Reliability

To date, onsite safety and reliability have been reasonably high with the existing treatment system. The valves used to seal the inlet and discharge ports of the canisters are very reliable. In addition, the contents of the canister are under very little pressure, approximating atmospheric pressure.

Future canister handling at the sites and round-trip transcontinental shipping to Pennsylvania for reactivation may pose problems with safety and reliability. Fork truck handling on and off the trucks for 4,100-lb canisters at the rate of 2 to 54 per day may become a major hazard, especially during snowy and icy weather. The maximum rate is equivalent to 4.5 truck loads per day. Potential spills or delays en route to or from Pennsylvania due to an accident or weather could make it difficult to meet the required total operating efficiency (TOE). Exposure of the public to possible spilled materials along the route is an issue that would be magnified if the material originated at a DOE nuclear facility such as the Hanford Site.

G.6.1.8 Compatibility with Existing Facilities

Since the baseline treatment system is already implemented, it is, by definition, an integral part of the existing facilities. Therefore, the system is totally compatible with existing facilities.

G.6.1.9 Construction and Operating Costs

Because the baseline treatment system is already implemented, there are no incremental construction costs. It is assumed that there is no onsite maintenance and that labor and equipment costs for onsite canister handling are included in the VES operating costs. Therefore, the carbon tetrachloride treatment cost for the baseline system is the price charged by Envirotrol for offsite GAC reactivation. Using the assumed GAC loading of 0.25 lb of carbon tetrachloride per pound of GAC and the contracted reactivation charge of \$1.42/lb of GAC results in a cost of \$5.68/lb of carbon tetrachloride treated.

G.6.2 THERMAL OXIDATION

Thermal oxidation is commonly applied in industry to destroy VOCs in contaminated air streams. It is included here because it was the lowest cost alternative in a previous report (WHC 1993) that evaluated treatment alternatives for the Carbon Tetrachloride ERA. It provides a cost comparison for the condensing alternatives. The following sections discuss the factors involved in deploying thermal oxidation as an alternative treatment system for onsite destruction of carbon tetrachloride extracted by the VES during operation of the 200 West Area Carbon Tetrachloride ERA. Section G.6.2.1 provides a process description of this technology as it would be applied to the ERA. Comparison factors described in Sections G.6.2.2 through G.6.2.9 include ARARs, development status, implementation schedule, secondary waste, operation and maintenance complexity, safety and reliability, compatibility, and cost.

The following discussion reflects use of thermal oxidation treatment configured in a single system at a single site. thermal oxidation would be able to destroy at least 99% of the 1,000 to 30,000 ppm_v of carbon tetrachloride contained in soil vapor. A GAC treatment train would be required downstream for thermal oxidation as a polishing process for normal operation with 10,000 and 30,000 ppm_v inlet concentrations to reach an exhaust to atmosphere concentration of 10 ppm_v.

G.6.2.1 Process Description

Thermal oxidation is a treatment process in which the carbon tetrachloride contaminant in the influent gas stream is oxidized at high temperature to carbon dioxide and hydrochloric acid. Carbon tetrachloride destruction efficiencies of 99% or higher are possible if the oxidation is carried out at 1,800 to 2,000 °F and ample residence time and turbulence are allowed. The hydrochloric acid that is formed would be treated by a neutralization process before the gas stream can be emitted.

Carbon tetrachloride is nonflammable and has a low heating value. Therefore, a supplemental energy source such as propane or electric heating

must be used to maintain the operating temperature at an inlet concentration of 1,000 ppm_v. The heat in the treated gas stream would be 98% recovered through regenerative heat exchange by means of a silica gravel bed contained within the oxidizer. Approximately 45,000 Btu/h (13 kW) would be required to provide the 2% not recovered during operation. Figure G-2 shows a schematic diagram of the proposed process. The thermal oxidation unit would require only electrical energy. Thermal oxidation units using propane as the energy source were evaluated but discarded because of higher capital and operating costs, greater process complexity, and the need to supply propane as fuel. At thermal oxidation outlet concentrations above 10 ppm_v as expected for all inlet concentrations above 1,000 ppm_v, the scrubber baghouse offgas with residual hydrochloric acid and carbon tetrachloride would be passed through the GAC to reach the 10 ppm_v emissions concentration. Hydrochloric acid corrosion problems may arise for the existing epoxy-lined carbon steel canisters with aluminum quick-disconnect fittings. Scrubber materials of construction would be selected for suitable corrosion resistance.

The thermal oxidation system would consist of a well-insulated cylindrical chamber filled with silica gravel. Electrical resistance heaters would be mounted in the center of the bed. Located above and below the bed would be plenum chambers, gas duct passages, and automatically operated valves that would allow the direction of process gas flow through the bed to be reversed at intervals of several minutes.

Air carrying carbon tetrachloride would enter one end of the silica bed and approach the heating elements. The silica gravel, which would be maintained at 1,800 °F, would rapidly heat the gas. The water in the stream would react with the carbon tetrachloride, oxidizing 99% or more of it to carbon dioxide and hydrochloric acid. Water vapor would be added to supplement the soil gas water vapor for inlet carbon tetrachloride concentrations above 2,000 ppm_v. This water vapor would be added at an as yet undetermined point by an undetermined means. The heat released by oxidation of carbon tetrachloride would raise the temperature of the gas stream by 10 to 300 °F.

After combustion, the exit portion of the silica bed would be heated by the exhaust gas stream that would rapidly cool to approximately 40 °F above the inlet temperature. In order to recover the heat stored in the bed, the gas flow direction would be reversed at regular intervals by the automatic valves on the gas ducts. A flow reversal would be activated by a preset bed exit temperature and typically would occur at intervals of 1 to 8 min. Flow reversal would maintain a uniform temperature distribution throughout the silica bed and conserve electrical energy needed to sustain the oxidation reaction by reusing the heat stored by the bed.

To maximize carbon tetrachloride destruction, it would be necessary to limit the quantity of desorption gas bypassing the silica bed during the flow reversal process. This would be achieved by using an automated valve to replace inlet soil vapor with clean, ambient air just prior to and during the reversal step. The clean air would sweep any residual carbon tetrachloride through the 1,800 °F oxidation zone for destruction before venting. After flow reversal was completed, soil vapor would again enter the fan and silica bed.

Figure G-2. Thermal Oxidation Process Flow Diagram.

The silica bed would ensure the uniformity of the gas stream flow through the bed by providing a relatively large pressure drop. Simultaneously, it would cause excellent mixing of the gas stream components to promote heat exchange with the bed and efficient oxidation of the carbon tetrachloride. The large heat capacity of the silica bed relative to the gas stream would allow it to retain heat and rapidly heat the incoming gas stream and cool the exiting gas stream. The silica bed would perform the dual functions of reactor and heat exchanger.

Removal efficiencies of 99.99% for carbon tetrachloride have been achieved in pilot-scale testing but have not been reported commercially. The well-insulated bed would require a day of startup time to achieve operating temperature. After reaching that temperature, it would be immune to thermal upset. No external heat exchanger would be needed, but a fan would be required to supply approximately 25 inH₂O pressure drop through the unit. The pressure drop would include 17 inH₂O of water through the silica bed and 8 inH₂O of water through the dry vent scrubber and baghouse. At 10,000 and 30,000 ppm_v, a wet slurry cyclone dryer would be required to remove the 10 to 30 times higher hydrochloric acid concentration. The unit would be skid mounted and would require electricity and some water for the slurry.

Thermal oxidation of carbon tetrachloride would generate hydrochloric acid, which would have to be treated. The thermal oxidation exit stream would be at approximately 40 °F above the inlet temperature and have a hydrochloric acid concentration proportionate to the carbon tetrachloride inlet concentration and a 99% conversion efficiency. Wet scrubbing of the exit stream was considered at inlet concentrations above 2,000 ppm_v, even with the difficulties of providing water to the site. Dry scrubbing was selected as the neutralizing process at lower inlet concentrations. Dry scrubbing would offer process simplicity and ease of dealing with the dry secondary waste. A scrubber would be provided as an integral part of the thermal oxidation process.

As shown in Figure G-3, the dry scrubber system would consist of a chemical receiving and storage system, a metering and transport system, a scrubber where the dry chemical and the hydrochloric acid contaminated exhaust gas from the thermal oxidation unit are brought into contact, a baghouse filter, and a secondary waste chemical transport and temporary storage system. The slurry cyclone dryer is not shown. The scrubber duct and baghouse would provide mixing and time for reaction of the contaminant gas and dry chemical along with separation of the dry chemical from the cleaned air before discharge through a stack. The stack would be equipped with a continuous hydrochloric acid concentration monitor. For overall simplicity, the dry scrubber and baghouse pressure drop of 8 inH₂O would be provided by the thermal oxidation system blower. Additional fan capacity would be needed for a wet slurry scrubber and also would be provided by the thermal oxidation blower.

The specifics of each of the above major subsystems could take a variety of forms and incorporate several important features to provide a continuous flow of chemicals at a controlled rate and to prevent chemical spills or emissions, overfill, and equipment plugging. Some features would depend on the scrubbing chemical selected and some would be required on all systems. Two examples of features needed by all systems are a control panel for transferring fresh chemical into storage and an air compression system to provide air for reverse pulse jet cleaning of the filter bags.

Figure 6-3. Dry Scrubbing Process Flow Diagram.

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Centimeter

Inches

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6 of 6

G.6.2.2 Ability to Satisfy ARARs

Assuming that a 10 ppm_v carbon tetrachloride outlet concentration is required, the thermal oxidation technology would meet all ARARs, provided GAC is used for polishing at inlet concentrations above 1,000 ppm_v and dry scrubbing is included to effectively neutralize hydrochloric acid.

Discharge of carbon tetrachloride would be limited to the residual not adsorbed by the GAC. Up to 9 lb/day of carbon tetrachloride would be emitted in the vent stream to the atmosphere. Air dispersion modeling performed as part of a previous analysis (DOE-RL 1991) estimated that 15 lb/day would result in 0.00714 µg/m³ annual average carbon tetrachloride concentration at the Hanford Site boundary. This is an order of magnitude below the acceptable source input level (ASIL) in Table G-1 for carbon tetrachloride of 0.067 µg/m³.

One ARAR related to the dry scrubber system is the requirement for less than 4 lb/h hydrochloric acid in air emissions from thermal oxidation systems. The hydrochloric acid removal would have to be at least 90% to meet a maximum emission of 4 lb/h of hydrochloric acid with an inlet concentration of 34.3 lb/h associated with a 990 ppm_v conversion from carbon tetrachloride. This degree of removal is achieved routinely in commercial applications using the dry scrubbing technology described above. Above 2,000 ppm_v inlet carbon tetrachloride, a wet slurry scrubber (not shown in Figure G-2) would be required.

The other ARAR related to the dry scrubber is the requirement of the ASIL for hydrochloric acid concentration not to exceed 23.3 µg/m³ 24-h average at the maximum concentration location on the Hanford Site boundary. A previous analysis (DOE-RL 1991) estimated that 4 lb/h of hydrochloric acid emitted from each of two systems would result in a 24-h average hydrochloric acid concentration of 1.484 µg/m³ at the maximum concentration location on the Hanford Site boundary. This value is an order of magnitude less than the maximum value specified for the ASIL in Table G-1.

The dry chemical injected in the scrubber is a powder in which, typically, 70% to 90% of the particles are less than 45 µm in diameter. The baghouse would have a maximum outlet particulate concentration of 0.015 grains/standard ft³ as determined by EPA Method 5. The thermal oxidation system outlet temperature would be in the range of 50 to 150 °F. The moisture from an all electric thermal oxidation process in which no propane is burned would be limited to that in the VES soil vapor. Since a 60% relative humidity and 80 °F temperature are assumed for the VES exit gas, the water vapor input to the thermal oxidation unit would be 87.8 lb/h. This quantity would be reduced at the thermal oxidation outlet by the carbon tetrachloride conversion to hydrochloric acid and carbon dioxide.

G.6.2.3 Technical Development Status

Standard thermal oxidation systems using supplemental fuel combustion as the source of heat have been used in environmental remediation for over 20 years to destroy gas phase contaminants. Improvements in technology have boosted removal efficiencies to 99% for many contaminants. However, greater efficiencies require exponentially larger dollar expenditures for achieving

higher temperatures and longer residence times. Applications requiring removal efficiencies much greater than 99% generally use other technologies. Use of GAC for polishing the thermal oxidation offgas is proposed for inlet concentrations up to 30,000 ppm_v where 99.97% removal efficiency is required.

The thermal oxidation process proposed here for the ERA treatment system uses electrical heaters, rather than fuel combustion to provide thermal energy. This electrically heated silica bed unit has been used in Europe for 10 years and has a 4-year operating history in the United States, mostly in oxidizing VOCs liberated by various soil remediation projects. It has shown promise in pilot-scale testing of boosting removal efficiencies to 99.99% for carbon tetrachloride; however, such high removal efficiencies have not been reported on a commercial scale. The improved removal efficiency is attributed to thorough mixing and uniformity of temperature provided by the silica bed.

The discussion of thermal oxidation technology presented in this report is based on a thermal oxidizer marketed as the RETOX 1500. RETOX is an acronym for REgenerative Thermal OXidizer. The device is manufactured by the Airex Corporation through license from ABB Air Preheater for treating soil vapor emissions. RETOX is the only known source for a unit of the size required for the Carbon Tetrachloride ERA application.

Dry scrubbing is a well understood and commonly used technology for removing acidic compounds from a process gas. The equipment that would be used to make up the scrubber and related systems is well developed and has been used for many years in large and small manufacturing and power generation systems. Many suppliers can provide the receiving, storage, metering, transport, and baghouse components. A small number of suppliers can provide the scrubber where the chemical and the gas are contacted.

Dry scrubbing technology is well developed for some chemicals, relative humidity ranges, and temperature ranges. Data for scrubbing hydrochloric acid with the low moisture concentration and temperature estimated for the Carbon Tetrachloride ERA thermal oxidation application indicate that hydrated lime would not be an appropriate choice for a scrubbing chemical. The systems where hydrochloric acid is scrubbed with lime typically operate at higher inlet temperature and water vapor concentrations since the scrubber inlet gas typically derives from incinerators and coal fired electric power generation facilities. Therefore, trona, a natural sodium sesquicarbonate, would be used for scrubbing hydrochloric acid produced by the thermal oxidation systems in this alternative.

G.6.2.4 Implementation Schedule

The thermal oxidation systems would take 9 to 12 months to implement. This includes 3 to 6 months to deliver the treatment equipment after receipt of order, 1 month for equipment installation, and 4 to 5 months for technology evaluation, request for bids, bid evaluation, and internal and regulatory agency approvals.

G.6.2.5 Secondary Waste Issues

There would be no water effluent from this system. The only secondary waste would be the solid powder resulting from the dry scrubbing neutralization of the hydrochloric acid. At a carbon tetrachloride concentration of 30,000 ppm_v, it is estimated that the thermal oxidation system would require up to 8,750 lb/h trona and would produce up to 12,300 lb/h of hazardous composed of secondary waste. The waste would be sodium chloride plus inert materials and unreacted trona. The least costly sample analysis and disposal would be by truck to Washougal, Washington for sample analysis and then to Arlington, Oregon for disposal. A 20-ton covered rolloff box would be filled in as little as 3 h. Up to eight truckloads would ship from the thermal oxidation system every day. A spare rolloff box at the scrubber would provide adequate time for delays in shipping due to weather or other factors only for an inlet concentration of 1,000 ppm_v. Both the active and the spare rolloff boxes would roll on wheels guided by inverted channels on the concrete slabs. The haul truck would be equipped to roll on a full box and to roll off an empty box.

Since trona and sodium chloride are not deliquescent, no handling problems are anticipated. Corrosion of steel, especially stainless steel, by chlorides is well known. An effective epoxy coating on carbon steel would be the preferred construction material.

G.6.2.6 Operating and Maintenance Complexity

There is expected to be little operating and maintenance complexity. All systems may be interlocked to fail in a safe mode should the VES, the thermal oxidizer, or the dry scrubber fail. No adverse consequences would result other than downtime to remedy the failed condition.

Operation would be very simple. It is expected that the process would operate unattended for a period of several hours. No special training, other than routine knowledge of the process and equipment, would be required of the operators.

The expected lifetime of the thermal oxidation heating elements is 1 year. They are easily replaced in the field in one day at a cost of approximately \$2,000. Routine operation and maintenance is expected for such items as gas duct valves, air compressor, rotary valves, blowers, and motors. Routine verification and maintenance of all control systems and instrumentation would be performed as well as inspections for corrosion around the thermal oxidizer and gas scrubber.

The scrubber and associated equipment would be designed for operation 24 h/day and 250 day/yr with two shifts per day unattended and one shift attended for limited preventive maintenance and performance checks. Although the dry scrubber and associated equipment for chemical supply and secondary waste would be complex, they would have low operating and maintenance requirements. No scrubber components would be scheduled for replacement during the planned 4-year operating life. A TOE of greater than the targeted 68% would

be expected. Response to out of limit control signals and limited preventive maintenance would be the only maintenance actions required on a routine basis.

At inlet concentration of 1,000 ppm_v, the thermal oxidation system would be expected to require less operator time than the baseline treatment systems. No fork truck handling of any GAC-filled canisters or equipment would be required. A fork truck might be needed from time to time to push the full rolloff box away and push the spare box into place. The primary operating labor would be associated with receiving dry scrubbing chemical and shipping solid secondary waste. Again, for 1,000 ppm_v inlet, the chemical would be received in about 29 loads/yr at 60,000 lb/load. The secondary waste would be shipped in about 62 loads/yr at about 40,000 lb/load. On average, this would be about two loads per week and would be expected to require about 5 h/week of operator time.

G.6.2.7 Safety and Reliability

Thermal oxidation is a proven technology. Safety and reliability could be expected to be very high. Likewise, the dry scrubber system is a proven technology with high reliability and safety. Interlocks would have to be incorporated to shut all systems down safely in the event of a component failure to prevent accidental emissions of carbon tetrachloride or hydrochloric acid. Shutdown of all blowers will prevent any gaseous emissions. The trona scrubbing chemical would be a slightly caustic, nontoxic material and would have to be handled appropriately by personnel. Neither the fresh chemical nor the spent waste would be explosive. Other standard features such as fire and radiological protection and warning would be included in the system.

Trona, a natural mineral composed of sodium carbonate and sodium bicarbonate with two waters of hydration, has been selected as the chemical for dry scrubbing. Based on data for sulfur dioxide, a two to five ratio to stoichiometric would be required with hydrated lime, calcium hydroxide, at the low moisture content estimated for the ERA soil vapor and the hydrochloric acid resulting from thermal oxidation. Also, the deliquescence of calcium chloride resulting from dry scrubbing with hydrated lime would have the potential for producing mud and plugging the baghouse and secondary waste transport equipment. These problems would be avoided with trona. For trona, the ratio in excess of stoichiometric rises as dry scrubbing temperature falls. Based on scrubber supplier recommendations, a ratio of 1.7 was assumed.

G.6.2.8 Compatibility with Existing Facilities

No incompatibility with existing facilities and operations would be expected with the thermal oxidation treatment systems. Electric power is the only energy used by the system and is readily available at the site. Trucking fresh trona to the site and spent trona away from the site would impose only a small increase in traffic at 1,000 ppm_v inlet carbon tetrachloride concentration. The bulk supply trucks would be pneumatically unloaded. The bulk rolloff box waste containers would be fully loaded and then trucks would winch them on for transport to offsite disposal. Load frequency and size are listed in Section G.6.2.6.

Direct, computerized control with signal transmission by telephone lines would provide for remote monitoring. Electric power supply at one of the proposed sites would be increased if necessary to meet the need for a 188-kW connected load.

G.6.2.9 Construction and Operating Costs

Construction costs for the thermal oxidation system include the oxidizer, dry scrubbers and baghouses, chemical storage, and waste storage. The treatment cost for the proposed thermal oxidation system, which includes operating costs, is \$2.54/lb to \$3.41/lb of carbon tetrachloride destroyed. At 1,000 ppm_v inlet concentration, \$2.54/lb is the second lowest cost among the alternatives evaluated. It is less than 45% of the baseline offsite GAC reactivation cost of \$5.68/lb of carbon tetrachloride destroyed. At inlet concentrations of 10,000 ppm_v and above, GAC reactivation and a wet slurry dryer make the thermal oxidation estimated cost higher than liquid nitrogen refrigeration.

Scrubber installation would consist of crane or forklift unloading of major modules from flatbed trucks and anchoring them to preplaced reinforced concrete slabs. The three large modules would be the wet slurry dryer, the chemical storage bin, and the baghouse. The other three modules would be on skids or be attachments to the baghouse. The chemical metering and transport system with the control panel could be skid mounted beside the storage bin. The dry scrubber duct would be used to connect the thermal oxidation system to the baghouse. The discharge stack and elbow would be field connected to the baghouse. The rolloff box cover with an integral distributing auger conveyor would be attached to the baghouse discharge device. The entire system would fit on a slab 20 by 80 ft. Prefabricated and pretested piping would be used to interconnect the modules. Electric power would be connected to a single point power and control panel. All subpanels would be field connected with factory fabricated wiring.

At 1,000 ppm_v, the estimated installed cost for the thermal oxidation system would be \$888,000. This total would include all of the equipment mentioned above along with associated infrastructure and services such as engineering.

The operating costs for the thermal oxidation system include electrical power and chemical purchase. The dry scrubber would require trona to neutralize the hydrochloric acid generated by oxidation. Spent and unreacted trona would be disposed as solid secondary waste. Heating elements would have to be replaced approximately once per year at a cost of about \$2,000.

The estimated annual operating cost of \$312,000 at 1,000 ppm_v inlet includes the cost for operating the thermal oxidation and scrubbing systems. It is comprised of labor, maintenance materials, electric power, and fresh trona. Secondary waste costs of \$246,000/yr would be for hauling and disposing 1,230 tons of solid hazardous waste composed of sodium chloride, inert material mined as part of the trona, and unreacted trona.

G.6.3 CONDENSATION BY MECHANICAL REFRIGERATION

Condensation by mechanical refrigeration would be able to recover in liquid form up to 99.97% of the carbon tetrachloride in the soil vapor of the Carbon Tetrachloride ERA. This degree of removal would be accomplished when soil vapor is at a carbon tetrachloride concentration of 30,000 ppm_v. Mechanical refrigeration would be used to compress, condense, and evaporate a nonchlorofluorocarbon refrigerant in a system of heat exchangers and controls and thereby liquify, freeze, and reliquify carbon tetrachloride, water, and other condensibles from the soil vapor. The entire soil vapor stream temperature would be lowered to the range of -40 °F to -103 °F, depending on the system configuration. This system would be located in the 200 West Area of the Hanford Site. The cleaned air discharging from the condensing system to the polishing or standby GAC would contain from 10 to 1,000 ppm_v, depending on the configuration adopted for this alternative. The cleaned air would always discharge from the GAC at the design value of 10 ppm_v.

The following sections describe the mechanical refrigeration process and three alternative configurations in detail. A process description of this treatment technology is provided in Section G.6.3.1. Sections G.6.3.2 through G.6.3.9 describe features that would be associated with or derived from the technology and compare those features with similar aspects of the baseline GAC reactivation alternative.

G.6.3.1 Process Description

One possible configuration of the alternative using mechanical refrigeration for condensation of carbon tetrachloride is shown in Figure G-4. This two-stage system would be able to produce a -40 °F temperature and a corresponding 3,000 ppm_v outlet concentration. A similar three-stage system would be used to produce -64 °F or -103 °F with corresponding outlet concentrations of 1,000 ppm_v and 100 ppm_v, respectively.

The feed to the system would be soil vapor from the VES. In addition to carbon tetrachloride, soil vapor would contain water vapor and traces of other VOCs including chloroform and 2-butanone. The water vapor is equivalent to 87.8 lb/h and results from assuming soil vapor exits the VES at a moisture vapor concentration equivalent to 60% relative humidity and 80 °F.

The utility required for process operation is electrical power. A defrost and low-temperature heat transport liquid such as d-limonene would be required in small quantities in some concepts.

In addition to piping, controls, and valves (not shown), the major components in the system are two or three compressors, an air-cooled condenser, a subcooler/superheater, and liquid refrigerant receiver, and two or three heat exchangers with liquid drain pans that take the reliquified condensate to a skid-mounted holding tank with pump. Electrical power consumption may be reduced by use of a cooling recovery heat exchanger (not shown). Based on supplier recommendation, an effectiveness of 70% of the dry air heat was assumed. Another important function of the cooling recovery heat exchanger is tempering the outlet air to a temperature compatible with the downstream polishing or standby GAC.

Figure G-4. Mechanical Refrigeration Condensation Process Flow Diagram.

Heat exchanger (HX) 2, the low-temperature heat exchanger where carbon tetrachloride is condensed and frozen at -9°F , is divided into two equal coils in an insulated and divided cabinet. Continuous operation is maintained by condensing in one half and defrosting in the other half of this heat exchanger. For example, liquid refrigerant enters and evaporates as it flows through HX-2A to condense carbon tetrachloride. Hot refrigerant gas from the discharge of the compressors would simultaneously flow through HX-2B to defrost and reliquify the frozen carbon tetrachloride. Intermediate temperature gas from between the compressors would flow through HX-1 to cool the soil vapor while avoiding ice formation.

G.6.3.2 Ability to Satisfy ARARs

The condensation by mechanical refrigeration system would be designed to meet the ARARs. The combination of mechanical refrigeration and standby GAC-filled canisters would remove 99% to 99.97% of the inlet carbon tetrachloride at soil vapor concentrations of 1,000 ppm_v to 30,000 ppm_v for a maximum discharge concentration of 10 ppm_v in the clean air. Mechanical refrigeration could be designed for a range of outlet concentrations to the polishing GAC down to the economic limit of about 100 ppm_v at -103°F used in this report. The GAC reactivation process would continue to produce additional emissions to the air. The secondary waste liquid would contain only those constituents that would desorb from the GAC, primarily carbon tetrachloride and water. Because there would be no conversion of carbon tetrachloride to hydrochloric acid, no hydrochloric acid would be discharged. This would ensure meeting the ARAR of 4 lb/h hydrochloric acid emissions and the ASIL of $0.067\text{ }\mu\text{g}/\text{m}^3$ hydrochloric acid concentration at the Hanford Site boundary.

G.6.3.3 Technical Development Status

Although none of the unit processes associated with mechanical refrigeration are new, the system combines the elements in a new design to effect the recovery of carbon tetrachloride. Based on information from two suppliers there are at least 430 systems in operation on VOCs in the United States. They routinely achieve 95% to 99% removal of compounds such as methylene chloride, gasoline, carbon tetrachloride, xylene, and methyl ethyl ketone at temperatures of -20°F to -100°F , depending on specification.

G.6.3.4 Implementation Schedule

Startup within 1 year is feasible since delivery is quoted for 14 to 16 weeks after order. Installation and acceptance tests could be completed within 2 weeks after arrival of equipment on site. However, it is not possible to predict the schedule impact associated with obtaining DOE and regulatory agency approvals prior to placing an order for a mechanical refrigeration system.

G.6.3.5 Secondary Waste Issues

At carbon tetrachloride concentration in the soil vapor of 30,000 ppm_v and depending on system configuration, and condensing temperature, it is

estimated that the mechanical systems would condense up to 31,300 lb/day, equivalent to 2,430 gal/day of carbon tetrachloride and water, at 12.9 lb/gal. A truckload of this mixture would accumulate in about 2 days. A 7,500-gal onsite storage tank has been assumed to provide adequate time for shipping delays due to weather or other factors. No pumping or corrosion problems would be anticipated.

G.6.3.6 Operating and Maintenance Complexity

While the mechanical refrigeration system is complex in terms of number of components, none of the components would be expected to need replacement during the planned 4-year operating life. A TOE of greater than 68% would be expected. This system is anticipated to have the third lowest scheduled operating maintenance requirement of any of the alternative vapor treatment systems including the baseline system. Thermal oxidation would have the highest operating maintenance requirements and the baseline system second highest. Compared to the baseline, little or no onsite fork truck loading and unloading of GAC-filled canisters would be required for 10,000 and 30,000 ppm_v inlet carbon tetrachloride concentrations. At 1,000 ppm_v inlet and condensers designed for -40 or -62 °F condensing temperature, equivalent to 3,000 and 1,000 ppm_v outlet to the polishing GAC, no condensation would occur and all carbon tetrachloride would be adsorbed by GAC. At -103 °F condensing temperature equivalent to 100 ppm_v into the polishing GAC, secondary waste liquid would be pumped and hauled by tank trucks at nominal 2-week intervals for a total of up to 20 loads per year. The 20 loads per year would occur at 1,000 ppm_v inlet and -103 °F condensing temperature. No condensation and no loads would be required for condensers designed to output 3,000 and 1,000 ppm_v into the polishing GAC with 1,000 ppm_v in the soil vapor. Only response to out-of-limit control signals and limited preventive maintenance would be anticipated.

G.6.3.7 Safety and Reliability

Most components such as piping and heat exchangers would have no moving parts. The valves and pumps would have few moving parts and would be designed and constructed to provide many years of service based on extensive industrial experience with similar equipment. Instrumentation and control components would be rated NEMA type 4 or 4X for reliable operation in the outdoor location.

G.6.3.8 Compatibility with Existing Facilities

Direct compatibility with existing facilities and operations would be provided by designing for appropriate hoses from the VES and to the GAC-filled canisters. Computerized control would allow the required level of compatible interface with the present and planned monitoring systems. Electric power supply at the existing site may not need to be increased to meet the need for the connected load. A new power supply could be added at any site without one.

G.6.3.9 Construction and Operating Costs

Budgetary quotes for this system were used to develop these estimates. Installation of the system would consist of crane or forklift unloading a skid-mounted module from a truck and anchoring it to a preplaced reinforced concrete slab. Each module would contain all components except the GAC canisters, the VES, and the connecting hoses. Electric power at 130 to 220 kW and 480 V would be connected to a single point power and control panel. Piping for hazardous secondary waste liquid to the adjacent temporary storage tank would be installed. The total installed cost of \$1,038,000 to \$1,513,000 would include all of the above along with associated infrastructure and services.

The estimated annual operating cost of \$75,000 to \$192,000 depends on configuration and soil vapor carbon tetrachloride concentration and is composed of labor, maintenance materials, and electric power. Secondary waste costs of \$56,000/yr to \$2,073,000/yr would be for hauling and reactivating GAC and hauling and disposing liquid hazardous waste composed of carbon tetrachloride and water. The assumed disposal incinerator is in Arkansas. There is an alternative hazardous waste incinerator in Texas. If the carbon tetrachloride quality permits, it may be possible to use it onsite and reduce the cost of disposal.

G.6.4 CONDENSATION BY LIQUID NITROGEN

Condensation by liquid nitrogen would be able to recover in liquid form 99% to 99.97% of the carbon tetrachloride in the soil vapor discharged by the VES at the Carbon Tetrachloride ERA. Removal of 99.97% would be accomplished when soil vapor is at a carbon tetrachloride concentration of 30,000 ppm_v. Liquid nitrogen refrigeration would be used in a system of heat exchangers and controls and thereby liquify, freeze, and reliquify carbon tetrachloride, water, and other condensibles from the soil vapor. The entire soil vapor stream temperature would be lowered to the range of -62 to -134 °F, depending on the system configuration and control settings. The main variation in configuration would be heat exchanger size and insulation quality. This system would be located in the 200 West Area of the Hanford Site. The cleaned air discharging from the condensing system to the polishing or standby GAC would contain from 10 to 1,000 ppm_v, depending on the configuration adopted for this alternative. The cleaned air would always discharge from the GAC at 10 ppm_v.

The following sections describe the liquid nitrogen condensation process in detail. A process description of this treatment technology is provided in Section G.6.4.1. Sections G.6.4.2 through G.6.4.9 describe features that would be associated with or derived from the technology and compare those features with similar aspects of the baseline GAC reactivation alternative.

G.6.4.1 Process Description

One possible configuration of the alternative using liquid nitrogen for condensation of carbon tetrachloride is shown on the schematic of Figure G-5.

The feed to the system would be soil vapor from the VES. In addition to carbon tetrachloride, soil vapor would contain water vapor and traces of other

Figure G-5. Liquid Nitrogen Condensation Process Flow Diagram.

VOCs including chloroform and 2-butanone. The water vapor is equivalent to 87.8 lb/m and results from assuming soil vapor exits the VES at a moisture vapor concentration equivalent to 60% relative humidity and 80 °F.

The liquid nitrogen would be piped to the adjacent heat exchanger and control skid and would enter HX-3. The liquid nitrogen refrigerant would be supplied by producers such as the one now supplying the Hanford Site. Bulk liquid trucks with 500,000-stdft³/min capacity would offload the liquid nitrogen into a bulk tank located on a concrete pad at the site at the rate of one to two loads per day. At 13.8 stdft³/lb and liquid density of 98.9 lb/ft³, these trucks will hold about 36,000 lb, equivalent to 2,700 gal. The other utility required for process operation is electrical power. A defrost and low-temperature heat transport liquid such as d-limonene would be required in small quantities in some configurations.

In addition to piping, controls, and valves (not shown), the major components in the system are three heat exchangers with liquid drain pans that take the reliquified condensate to a skid-mounted holding tank(s) with pump(s) for carbon tetrachloride, water, or combined condensates. There would also be a tank for condensed water in the concept shown. Nitrogen consumption may be reduced by use of a cooling recovery heat exchanger (not shown). An effectiveness of 70% of the dry air heat was used at the recommendation of the suppliers. Another important function of the cooling recovery heat exchanger is tempering the outlet air to a temperature compatible with the downstream standby GAC.

HX-2 and HX-3, the two low-temperature heat exchangers where carbon tetrachloride is condensed and frozen at -9 °F, are both divided into two equal coils in an insulated and divided cabinet. Continuous operation is maintained by condensing in one half and defrosting in the other half of these heat exchangers. For example, cold nitrogen flows through HX-2A and HX-3A to condense carbon tetrachloride. Warm nitrogen from the outlet of HX-1 or clean air from the discharge of HX-3A would simultaneously flow through HX-2B and HX-3B to defrost and reliquify the frozen carbon tetrachloride. The liquid nitrogen is vaporized to gas in HX-3. The gas is warmed in HX-2 to a temperature to avoid water freezing in HX-1.

G.6.4.2 Ability to Satisfy ARARs

The condensation by liquid nitrogen system would be designed to meet the ARARs. The combination of liquid nitrogen refrigeration and standby GAC-filled canisters would remove 99% to 99.97% of the inlet carbon tetrachloride at soil vapor concentrations of 1,000 ppm_v to 30,000 ppm_v for a maximum discharge concentration of 10 ppm_v in the clean air. Liquid nitrogen refrigeration could be designed for a range of outlet concentrations to the polishing GAC down to a few ppm_v as limited by liquid nitrogen temperature and cost. For this report, the range was 10 to 1,000 ppm_v into the polishing GAC. The GAC reactivation process would continue to produce additional emissions to the air. The secondary waste liquid would contain only those constituents that would desorb from the GAC, primarily carbon tetrachloride and water. Discharge of carbon tetrachloride would be limited to the residual not adsorbed by the GAC. Up to 9 lb/day of carbon tetrachloride would be emitted in the vent stream to the atmosphere. Air dispersion modeling performed as part of a previous analysis (DOE-RL 1991) estimated that 15 lb/day would

result in $0.00714 \mu\text{g}/\text{m}^3$ annual average carbon tetrachloride concentration at the Hanford Site boundary. This is an order of magnitude below the ASIL for carbon tetrachloride of $0.067 \mu\text{g}/\text{m}^3$. Because there would be no conversion of carbon tetrachloride to hydrochloric acid, no hydrochloric acid would be discharged. This would ensure meeting the ARAR of 4 lb/h hydrochloric acid emissions and the ASIL of $0.067 \mu\text{g}/\text{m}^3$ hydrochloric acid concentration at the Hanford Site boundary.

G.6.4.3 Technical Development Status

Although none of the unit processes associated with liquid nitrogen condensation are new, the system would combine the elements in a new design to effect the recovery of carbon tetrachloride. These systems routinely achieve buyer specified 98 to above 99% removal of compounds such as methylene bromide, methylene chloride, and gasoline at temperatures of -105 to -250 °F, depending on specification.

G.6.4.4 Implementation Schedule

Startup within 1 year is feasible since delivery is quoted for 14 to 16 weeks after order. Installation and acceptance tests could be completed within 2 weeks after arrival of equipment onsite. However, it is not possible to predict the schedule impact associated with obtaining DOE and regulatory agency approvals prior to placing an order for a liquid nitrogen system.

G.6.4.5 Secondary Waste Issues

Depending on carbon tetrachloride concentration in the soil vapor, system configuration, and condensing temperature, it is estimated that the liquid nitrogen systems would condense up to 32,200 lb/day, equivalent to 2,500 gal/day of carbon tetrachloride and water at 12.9 lb/gal. A truckload of this mixture would accumulate in about two days. A 7,500-gal onsite storage tank has been assumed to provide adequate time for shipping delays due to weather or other factors. No pumping or corrosion problems would be anticipated.

G.6.4.6 Operating and Maintenance Complexity

While the liquid nitrogen system is complex in terms of number of components, none of the components would be expected to need replacement during the planned 4-year operating life. A TOE of greater than 68% would be expected. This system is anticipated to have the lowest scheduled operating maintenance requirement of any of the alternative vapor treatment systems including the baseline system. Thermal oxidation would have the highest operating maintenance requirements and the baseline system second highest. Little or no onsite fork truck loading and unloading of GAC-filled canisters would be required for 1,000, 10,000, and 30,000 ppm_v inlet carbon tetrachloride concentrations except at 1,000 ppm_v inlet and -62 °F condensing temperature. At 1,000 ppm_v inlet and -62 °F, no condensation would occur and all carbon tetrachloride would be adsorbed by GAC. Nitrogen would be delivered at one or two loads per day by the same bulk liquid trucks that

presently deliver to multiple tanks on the Hanford Site. Secondary waste liquid would be pumped and hauled by tank trucks at as short as a 1.4-day interval for a total of up to 20 loads per year. The 20 loads per year would occur at 1,000 ppm_v inlet and -103 °F or -134 °F condensing temperature. No loads would be required for 1,000 ppm_v into the polishing GAC with 1,000 ppm_v in the soil vapor. Only response to out-of-limit control signals and limited preventive maintenance would be anticipated.

G.6.4.7 Safety and Reliability

Most components such as piping and heat exchangers would have no moving parts. The valves and pumps would have few moving parts and would be designed and constructed to provide many years of service based on extensive industrial experience with similar equipment. Instrumentation and control components would be rated NEMA type 4 or 4X for reliable operation in the outdoor location.

G.6.4.8 Compatibility With Existing Facilities

Direct compatibility with existing facilities and operations would be provided by designing for appropriate hoses from the VES and to the GAC-filled canisters. Computerized control would allow the required level of compatible interface with the present and planned monitoring systems. Electric power supply at the existing site would not need to be increased to meet the need for the connected load. A new power supply could be added at any site without one.

G.6.4.9 Construction and Operating Costs

Budgetary quotes for this system were used to develop these estimates. Installation of the system would consist of crane or forklift unloading of two skid-mounted modules from a truck and anchoring it to a preplaced reinforced concrete slab. Each module would contain all components except the GAC-filled canisters, the VES, and the connecting hoses. Electric power in the range of 10 kW and 480 V would be connected to a single point power and control panel. Piping for hazardous secondary waste liquid to the adjacent temporary storage tank would be installed. The total installed cost of \$850,000 to \$900,000 would include all of the above along with associated infrastructure and services.

The estimated annual operating cost of \$101,000 to \$976,000 depends on configuration and soil vapor carbon tetrachloride concentration and is composed of labor, maintenance materials, and electric power. Secondary waste costs of \$50,000/yr to \$2,123,000/yr for onsite and \$110,000/yr to \$2,073,000/yr for offsite would be for hauling and disposing liquid hazardous waste composed of carbon tetrachloride and water and hauling and reactivating GAC. The assumed disposal incinerator is in Arkansas. There is an alternative hazardous waste incinerator in Texas. If the carbon tetrachloride quality permits, it may be possible to use it onsite and reduce the cost of disposal.

G.7.0 ALTERNATIVE TREATMENT SYSTEM COSTS

It was determined that the three alternative carbon tetrachloride treatment systems and the baseline system would meet all ARARs including the outlet carbon tetrachloride concentration of 10 ppm_v established for this analysis. Therefore, it is assumed that the treatment cost will be the primary criterion in any decision to implement an alternative to the baseline treatment system. Section G.7.1 documents the methods used to estimate treatment costs for the alternative systems. Section G.7.2 compares the treatment cost for the baseline system with those estimated for the three technologies: mechanical refrigeration condensation, liquid nitrogen condensation, and thermal oxidation.

G.7.1 BASIS FOR ESTIMATED COSTS

This section describes the methods used to estimate costs for the baseline offsite GAC reactivation, and for the three alternative treatment systems in a total of seven configurations (two condensation alternatives in three configuration each plus the thermal oxidation alternative).

For all condensation and thermal oxidation technologies, the alternatives comparison was simplified by achieving an exhaust carbon tetrachloride concentration of 10 ppm_v. This is equal to a 99% carbon tetrachloride removal at 1,000 ppm_v inlet concentration and a 99.97% removal at 30,000 ppm_v soil vapor concentration.

Item 5 of Tables G-2, G-3, and G-4, presents the cost, in dollars per pound of carbon tetrachloride removed, required by each alternative. These costs are derived by multiplying the requirements for utilities, fuel, chemicals, and secondary waste disposal shown in the footnotes of Tables G-2, G-3, and G-4 by appropriate unit cost factors and then adding the costs for installation, operation, and maintenance. Implementing the existing baseline treatment system would require no additional equipment. In addition, the costs for removing, storing, and shipping loaded GAC canisters and for receiving, storing, and installing fresh GAC canisters are included in the VES operating costs. Therefore, treatment cost for the baseline system was derived directly by combining the carbon tetrachloride loading (i.e., the average GAC adsorption capacity) included in the design basis for this evaluation with the cost for reactivating 1 lb of GAC as specified by the existing contract with Envirotrol. Specifically, the assumed GAC loading of 0.25 lb of carbon tetrachloride per pound of GAC combined with the contracted reactivation charge of \$1.42/lb of GAC results in a cost of \$5.68/lb of carbon tetrachloride treated. Although loading up to 0.6 lb of carbon tetrachloride per pound of GAC can occur at 30,000 ppm_v inlet concentration, inlet concentration to the GAC is assumed to be limited to 3,000 ppm_v by dilution with outdoor air to avoid GAC overheating.

Treatment costs for the alternative, onsite systems were obtained by developing estimates for individual cost elements, using those estimates to obtain the EUAC for each alternative, and then dividing these EUACs by the total pounds of carbon tetrachloride to be treated annually. The EUACs and, thus, these results are specific to treating carbon tetrachloride from the VES at the Hanford Site operation of the 200 West Area Carbon Tetrachloride ERA.

Table G-2. Cost Estimate for 30,000 ppm_v Carbon Tetrachloride Concentration.

Alternative	Baseline GAC	Mechanical	Mechanical	Mechanical	Liquid	Liquid	Liquid	Onsite Thermal
Refrigerant	Offsite Thermal	R22/HP80	R22/HP80	R22/HP80	Nitrogen	Nitrogen	Nitrogen	Oxidation w/Dry
	HCl Scrubbing	2 Stage	3 Stage	3 Stage	Indirect	Indirect	Indirect	HCl Scrubbing
Outlet CCl ₄ concentration to polishing GAC, ppm _v	10	3,000	1,000	100	1,000	100	10	300
Condensing temperature, °F		-40	-62	-103	-62	-103	-134	
CCl ₄ heat load, Btu/hr		442,000	484,000	561,000	484,000	561,000	620,000	
Delivery from date of order, weeks		22	22	22	12	12	12	12
Item Parameter								
1 Installation costs [1]								
Electrical distribution, \$ [2]								
Condensing system, \$		405,000	485,000	595,000	330,000	340,000	350,000	535,000 [12]
Waste handling, \$ [3]		10,000	10,000	10,000	10,000	10,000	10,000	10,000
Total equipment cost, \$		415,000	495,000	605,000	340,000	350,000	360,000	545,000
Total installed cost, \$ [4]		1,038,000	1,238,000	1,513,000	850,000	875,000	900,000	1,363,000
2 Operating & maintenance (O & M) costs:								
Basic O & M, \$/yr [5]		73,000	87,000	106,000	60,000	61,000	63,000	95,000
Electricity, \$/yr @ \$0.06/MWh [6]		2,000	2,000	3,000	0	0	0	2,000
Liquid nitrogen, \$/yr @ \$0.45/100 scf [7]					41,000	49,000	55,000	273,000 [13]
Total O & M Cost, \$/yr		75,000	89,000	109,000	101,000	110,000	118,000	370,000
3 Waste disposal costs:								
Offsite waste, \$/yr [8]	1,988,000	300,000	198,000	133,000	198,000	133,000	128,000	404,000
Onsite use at Plutonium Finishing Plant (PFP), \$/yr [9]		235,000	124,000	56,000	124,000	56,000	50,000	
4 Treatment system equivalent uniform annualized cost (EUAC): [10]								
Offsite waste, \$/yr	1,988,000	702,000	678,000	719,000	567,000	519,000	530,000	1,204,000
Onsite use at PFP, \$/yr		637,000	604,000	642,000	493,000	442,000	452,000	
5 Treatment cost [11]								
Offsite waste, \$/lb CCl ₄	5.68	1.55	1.78	1.89	1.49	1.36	1.39	3.17
Onsite use at PFP, \$/lb CCl ₄		1.55	1.58	1.69	1.29	1.16	1.19	

Notes:

- [1] Design inlet vapor is HEPA filtered and composed of 1,500 scfm dry air, 30,000 ppm_v carbon tetrachloride, 2 V% water vapor, and less than 10 ppm_v of chloroform and 2-butanone, and less than 10 ppm_v total of other organic compounds.
Design inlet mass flows are 6,750 lb/hr air, 1,132 lb/hr CCl₄, and 87.8 lb/hr water.
- [2] Connected kW in Total Installed Cost factor, Note 4.
- [3] A blank indicates inclusion in the condensing system of a minimum 5,000 gal tank and 40 gpm pump.
- [4] Supplier quoted costs are multiplied by 2.5 as applicable to Hanford Site facilities on noncontaminated sites. See text.
- [5] Estimated at 1% of total installed cost per year for all onsite alternatives based on Hanford Site experience.
- [6] Operating power, Bhp
- [7] Liquid nitrogen, hundreds of scf/yr with recovery of 70% of air sensible cooling
- [8] Hazardous waste w/operation, 24 hr/day
- [9] Based on one operator, one shift, 2,080 hr/yr and one existing tank truck of 4,000 gal and 53,000 lb load.
- [10] EUAC equals (C 31547 x Item 1) ÷ Item 2 + Item 3 and is based on a 4 year life and a 10% discount factor.
- [11] Treatment cost equals EUAC/(2,000 x tons/yr CCl₄ from Note 8).
- [12] Includes the cost of THERMOX, HCl scrubbing, and scrubbing chemical storage and delivery.
- [13] Trona for HCl scrubbing, \$/yr
- [14] Trona for HCl scrubbing, tons/yr
- [15] Hazardous waste, sodium chloride and unreacted trona, tons/yr

Table G-3. Cost Estimate for 10,000 ppmv Carbon Tetrachloride Concentration.

Alternative:	Baseline GAC	Mechanical	Mechanical	Mechanical	Liquid	Liquid	Liquid	Onsite Thermal
Refrigerant:	Offsite Thermal	R22/HP80	R22/HP80	R22/HP80	Nitrogen	Nitrogen	Nitrogen	Onsite Thermal
	Oxidation w/Wet	2 Stage	3 Stage	3 Stage	Indirect	Indirect	Indirect	Oxidation w/Dry
	HCl Scrubbing							HCl Scrubbing
Outlet CCl ₄ concentration to polishing GAC, ppmv:	10	3,000	1,000	100	1,000	100	10	100
Condensing temperature, °F		-40	-62	-103	-62	-103	-134	
CCl ₄ heat load, Btu/hr		351,000	389,000	460,000	359,000	460,000	514,000	
Delivery from date of order, weeks		22	22	22	12	12	12	12
Item	Parameter							
1	Installation costs: [1]							
	Electrical distribution, \$ [2]							
	Condensing system, \$	405,000	485,000	595,000	330,000	340,000	350,000	535,000 [12]
	Waste handling, \$ [3]	10,000	10,000	10,000	10,000	10,000	10,000	10,000
	Total equipment cost, \$	415,000	495,000	605,000	340,000	350,000	360,000	545,000
	Total installed cost, \$ [4]	1,038,000	1,238,000	1,513,000	850,000	875,000	900,000	1,363,000
2	Operating & maintenance (O & M) costs							
	Basic O & M, \$/yr [5]	73,000	87,000	106,000	60,000	61,000	63,000	95,000
	Electricity, \$/yr @ \$0.06/kWh [6]	6,000	7,000	9,000	0	0	0	6,000
	Liquid nitrogen, \$/yr @ \$0.45/100 scf [7]				63,000	104,000	118,000	273,000 [13]
	Total O & M Cost, \$/yr	79,000	94,000	115,000	143,000	165,000	181,000	374,000
3	Waste disposal costs:							
	Offsite waste, \$/yr [8]	1,994,000	710,000	333,000	333,000	162,000	146,000	401,000
	Onsite use at Plutonium Finishing Plant (PFP), \$/yr [9]		649,000	249,000	249,000	67,000	50,000	
4	Treatment system equivalent uniform annualized cost (EUAC): [10]							
	Onsite waste, \$/yr	1,994,000	1,116,000	818,000	743,000	603,000	611,000	1,205,000
	Onsite use at PFP, \$/yr		1,055,000	734,000	655,000	508,700	515,000	
5	Treatment cost: [11]							
	Offsite waste, \$/lb CCl ₄	5.68	2.57	1.88	1.73	1.72	1.39	2.77
	Onsite use at PFP, \$/lb CCl ₄		2.43	1.69	1.52	1.53	1.17	1.18

Notes

- [1] Design inlet vapor is HEPA filtered and composed of 1,500 scfm dry air, 10,000 ppmv carbon tetrachloride, 2 V% water vapor, and less than 10 ppmv of chloroform and 2-butanone, and less than 10 ppmv total of other organic compounds. Design inlet mass flows are 6,750 lb/hr air, 377 lb/hr CCl₄, and 87.8 lb/hr water.
- [2] Connected kW, in Total Installed Cost factor, Note 4
- [3] A blank indicates inclusion in the condensing system of a minimum 5,000 gal tank and 40 gpm pump.
- [4] Supplier quoted costs are multiplied by 2.5 as applicable to Hanford Site facilities on noncontaminated sites. See text.
- [5] Estimated at 7% of total installed cost per year for all onsite alternatives based on Hanford Site experience.
- [6] Operating power, Bhp
- [7] Liquid nitrogen, hundreds of scf/yr with recovery of 70% of air sensible cooling. Trucks/day at 500,000 scf/truck
- [8] Hazardous waste w/operation, 24 hr/day. Quantity, tons/yr CCl₄ & H₂O, 2 days/truckload. Incineration site - Little Rock, AR at Quantity, containers/day GAC w/CCl₄ Quantity, GAC tons/yr + CCl₄ Disposal site - Sewickley, PA at
- [9] Based on one operator, one shift, 2,080 hr/yr and one existing tank truck of 4,000 gal and 53,000 lb load.
- [10] EUAC equals (0.31547 x Item 1) + Item 2 + Item 3 and is based on a 4 year life and a 10% discount factor.
- [11] Treatment cost equals EUAC/(2,000 x tons/yr CCl₄ from Note 8).
- [12] Includes the cost of THERMOX, HCl scrubbing, and scrubbing chemical storage and delivery.
- [13] Trona for HCl scrubbing, \$/yr
- [14] Trona for HCl scrubbing, tons/yr
- [15] Hazardous waste, sodium chloride and unreacted trona, tons/yr

Table G-4. Cost Estimate for 1,000 ppm_v Carbon Tetrachloride Concentration.

Alternative Refrigerant	Baseline GAC Offsite Thermal Oxidation w/Wet HCl Scrubbing	Mechanical R22/HP80 2 Stage	Mechanical R22/HP80 3 Stage	Mechanical R22/HP80 3 Stage	Liquid Nitrogen Indirect	Liquid Nitrogen Indirect	Liquid Nitrogen Indirect	Onsite Thermal: Oxidation w/Dry HCl Scrubbing
Outlet CCl ₄ concentration to polishing GAC, ppm _v	10	3,000	1,000	100	1,000	100	10	10
Condensing temperature, °F		-40	-62	-103	-62	-103	-134	
CCl ₄ heat load, Btu/hr		310,000	347,000	415,000	347,000	415,000	467,000	
Delivery from date of order, weeks		22	22	22	12	12	12	12
Item Parameter								
1 Installation costs [1]								
Electrical distribution, \$ [2]								
Condensing system, \$		405,000	485,000	595,000	330,000	340,000	350,000	345,000 [12]
Waste handling, \$ [3]		10,000	10,000	10,000	10,000	10,000	10,000	10,000
Total equipment cost, \$		415,000	495,000	605,000	340,000	350,000	350,000	355,000
Total installed cost, \$ [4]		1,038,000	1,238,000	1,513,000	850,000	875,000	900,000	888,000
2 Operating & maintenance (O & M) costs:								
Basic O & M, \$/yr [5]		73,000	87,000	106,000	60,000	61,000	63,000	62,000
Electricity, \$/yr @ \$0.06/kWh [6]		52,000	69,000	86,000	4,000	4,000	4,000	57,000
Liquid nitrogen, \$/yr @ \$0.45/100 scf [7]					667,000	796,000	909,000	193,000 [13]
Total O & M Cost, \$/yr		125,000	156,000	192,000	731,000	861,000	976,000	312,000
3 Waste disposal costs:								
Offsite waste, \$/yr [8]	2,073,000	2,073,000	2,073,000	523,000	2,073,000	523,000	358,000	246,000
Onsite use at Plutonium Finishing Plant (PFP), \$/yr [9]		2,123,000	2,123,000	215,000	2,123,000	215,000	50,000	
4 Treatment system equivalent uniform annualized cost (EUAC): [10]								
Offsite waste, \$/yr	2,073,000	2,525,000	2,520,000	1,192,000	3,072,000	1,660,000	1,528,000	838,000
Onsite use at PFP, \$/yr		2,575,000	2,670,000	884,000	3,122,000	1,352,000	1,310,000	
5 Treatment cost [11]								
Offsite waste, \$/lb CCl ₄	5.68	6.92	7.18	1.09	8.42	1.52	1.48	0.76
Onsite use at PFP, \$/lb CCl ₄		7.05	7.32	0.81	8.55	1.23	1.19	

Notes:

- [1] Design inlet vapor is HEPA filtered and composed of 1,500 scfm dry air, 1,000 ppm_v carbon tetrachloride, 2 V% water vapor, and less than 10 ppm_v of chloroform and 2-butanone, and less than 10 ppm_v total of other organic compounds. Design inlet mass flows are 6,750 lb/h air, 38 lb/hr CCl₄, and 87.8 lb/hr water.
- [2] Connected kW, in Total Installed Cost factor, Note 4
- [3] A blank indicates inclusion in the condensing system of a minimum 5,000 gal tank and 40 gpm pump.
- [4] Supplier quoted costs are multiplied by 2.5 as applicable to Hanford Site facilities on noncontaminated sites. See text.
- [5] Estimated at 7% of total installed cost per year for all onsite alternatives based on Hanford Site experience.
- [6] Operating power, Bhp
- [7] Liquid nitrogen, hundreds of scf/yr with recovery of 70% of air sensible cooling
- [8] Trucks/day at 500,000 scf/truck
- [9] Hazardous waste w/operation, 24 hr/day
- [10] Quantity, tons/yr CCl₄ & H₂O; 2 days/truckload
- [11] Incineration site - Little Rock, AR at
- [12] Quantity, canisters/day GAC w/CCl₄
- [13] Quantity, GAC tons/yr + CCl₄
- [14] Disposal site - Sewickley, PA at
- [15] Based on one operator, one shift, 2,080 hr/yr and one existing tank truck of 4,000 gal and 53,000 lb load
- [16] EUAC equals (0.31547 x Item 1) + Item 2 + Item 3 and is based on a 4 year life and a 10% discount factor.
- [17] Treatment cost equals EUAC/(2,000 x tons/yr CCl₄ from Note 8)
- [18] Includes the cost of THERMOX, HCl scrubbing, and scrubbing chemical storage and delivery
- [19] Trona for HCl scrubbing, \$/yr
- [20] Trona for HCl scrubbing, tons/yr
- [21] Hazardous waste, sodium chloride and unreacted trona, tons/yr

These estimated costs are considered to be budgetary quality and, based on Ebasco's experience and available information, they are within 20% of the expected actual costs. As presented here, these costs are suitable for comparative purposes only. Figure G-6 compares the estimated costs for the alternatives for offsite disposal and Figure G-7 compares the estimated costs for onsite use at PFP.

The three cost categories applicable to this comparative evaluation are listed below:

- Equipment installation costs
- Operating and maintenance costs
- Secondary waste disposal or use costs.

For each alternative carbon tetrachloride treatment system, these cost categories are combined to calculate an EUAC. A given EUAC is the direct sum of annual operating, maintenance, and secondary waste disposal costs plus a factor times the total installed cost. The factor accounts for the time value of money by spreading the installed equipment cost across the life of the project. In this case, the factor is derived based on a 4-year operating life and a 10% discount rate.

Total installed costs are a multiple of total equipment costs quotations provided in the first half of 1993 by vendors and developers who have installed and operated systems to treat carbon tetrachloride, or similar VOCs, and hydrochloric acid. These equipment costs include freight. The multiplier applied to the equipment costs to estimate installed costs includes the following:

- Handling, placement, and anchorage in the prepared location
- Washington State sales tax
- Infrastructure costs
- Project services costs.

Infrastructure costs include the concrete base pads and foundations, integration with and connection to the existing site instrumentation and control system, outside facilities, and auxiliary equipment. Project services costs include engineering, contract administration, and project management.

Figure G-6. Estimated Cost of Carbon Tetrachloride Disposal Offsite.

Figure G-7. Estimated Cost of Carbon Tetrachloride Use at Plutonium Finishing Plant.

Notes to Tables G-2, G-3, and G-4 define elements contributing to the overall multiplier. The following example illustrates the use of these elements:

	Cost (\$)	
Quoted Equipment Cost	100,000	A
Tax @ 7.8% of A	7,800	
Handling/Placement/Anchorage @ 21% of A	21,000	
Subtotal	128,800	B
Instruments/Controls @ 8% of B	10,300	
Outside Facilities @ 10% of B	12,900	
Auxiliary Equipment @ 5% of B	6,400	
Subtotal	158,400	C
Engineering @ 27% of C	42,800	
Contract Administration @ 16% of C	25,300	
Project Management @ 15% of C	23,800	
Total Installed Cost	250,300	

For this evaluation, the installed cost multiplier is estimated to be 2.5 times the equipment cost. This multiplier reflects the additional costs for infrastructure and services associated with standalone facilities such as the carbon tetrachloride treatment alternatives. A multiplier of similar magnitude has been developed through many years of experience at the Hanford Site as an effective order-of-magnitude cost estimating factor for Hanford Site standalone facilities. This multiplier was used recently to estimate the overall cost of a \$27 million Hanford Site waste treatment facility within 3% of the successful design/construct bid.

The 2.5 multiplier is based on installation in an open area having clean soil. It makes no allowance for safety analysis reports, State Environmental Policy Act or National Environmental Policy Act documentation, operating preparedness and startup analyses, quality assurance audits and surveillance, radiation safety monitoring and protection during construction, and hand excavation often associated with radiation zones. However, if any of these activities were required, the cost would be approximately equal for each of the seven alternative treatment systems configurations. Thus, the relative differences among the estimated treatment costs are valid for purposes of comparison.

All equipment associated with the alternative carbon tetrachloride treatment systems would be located outdoors on reinforced concrete slabs. Most of the equipment would be assembled in modules at fabrication shops and then mounted on skids or trailers for shipment to the site. Tall equipment such as baghouse filters would be shipped to the site on flatbed trucks and erected and anchored to concrete bases. Storage costs for hydrochloric acid neutralization chemicals and dry neutralization wastes, where applicable, are based on using 1,600-ft³, 60,000-lb capacity, four-hopper bulk trailers equipped for pneumatic filling and discharge. For each onsite treatment system, the equipment cost multiplier includes instruments and controls to monitor and control carbon tetrachloride concentration entering the process from the GAC desorption step. This multiplier also includes instruments and controls to monitor carbon tetrachloride and, where applicable, hydrochloric

acid concentrations in the process exhaust stack and to generate alarms or to shut down the process if preset limits are approached or exceeded.

Each alternative treatment system would be designed for 24 h/day, 5 day/week, 250 day/yr automatic, unattended operation. Beyond infrequent system startups and shutdowns accomplished by manual setting of controls, each system would require operator attention for a few hours per day to perform activities such as monitoring and adjusting equipment, handling loaded and reactivated GAC canisters, receiving process chemical shipments, and overseeing shipments of secondary wastes. In addition, each system would require attention by maintenance staff to perform unscheduled and preventive maintenance.

An annual operating and maintenance cost factor, estimated at 7% of total installed cost, is applied to the three treatment alternatives and the baseline system. This factor is specific to the Hanford Site based on historical data and includes estimated labor, materials, tools, equipment, and laboratory analysis required for normal operation and maintenance of particular systems. Applying the same factor to all treatment systems is warranted because the systems have comparable complexity when auxiliary facilities required for chemical feed and storage are considered in conjunction with the core treatment process. Comparison of mechanical refrigeration systems with the other alternatives can illustrate this concept. Mechanical refrigeration treatment is mechanically complex in terms of number of components and controls, but it has very simple chemical supply and waste handling facilities. Operating and maintenance costs for the baseline treatment system are incorporated in the VES operating costs. Therefore, no annual factor is applied to the baseline system.

The cost of liquid nitrogen is based on the assumption that the existing Hanford Site supplier would provide liquid nitrogen storage tanks at no additional cost and provide the incremental nitrogen at the current unit cost. These assumptions are based on current vendor practices when adding incremental chemical supply facilities.

Annual costs for operation and waste disposal are strongly affected by the number of 24-h days and the number of hours of operation as indicated in footnote 8 of Tables G-2, G-3, and G-4. In the range from 1,000 to 30,000 ppm_v carbon tetrachloride in the soil vapor from the VES and at an air flow of 1,580 stdft³/min, the total operating time would be 1,095 days (3 years) to 39 days of 24 h each. When these times are divided equally into 3 years, the carbon tetrachloride removal will be a nominal 170 tons/yr or a total 500 tons, the estimated extractable amount of the total estimated 1,100 tons disposed to the soil. These operating times are for comparison of alternatives only and include the range of concentrations experienced thus far. Actual average soil vapor concentration and resultant operating time will depend on many factors including vadose geology, weather, maintenance, and operating safety considerations.

Condensed water vapor is assumed to be a part of the total hazardous waste at a constant concentration in the soil vapor. At lower inlet soil vapor carbon tetrachloride concentrations, the condensed water will be a larger fraction of the waste. At 1,000 ppm_v, water is in the order of 70% of the waste. Thus, the hazardous waste liquid quantities are greater at lower carbon tetrachloride concentrations.

The process of estimating costs for secondary waste disposal involved three steps: (1) estimating the volume of waste, (2) projecting classification for the waste, and (3) multiplying the annual volume by the appropriate unit cost factor. The resulting annual disposal costs are included in the EUACs. The unit cost factors include the cost of transportation to disposal sites and the characterization (as appropriate for each type of material) to ensure that each shipment carries the correct classification. In each case, the volume of solid secondary waste was estimated from calculated weight and assumed bulk density. For the baseline treatment system, the entire treatment cost is included under secondary waste disposal. This is done for simplicity, even though 85% to 95% of the GAC would be returned to the Hanford Site after reactivation.

G.7.2 RESULTS OF COST COMPARISON

Individual elements contributing to the treatment costs calculated for the alternative systems are estimated and are characterized as budgetary quality. However, these estimates were obtained using the same basis for each alternative. Therefore, the alternative treatment costs are considered to be relative to each other for comparison purposes. Furthermore, the accuracy normally assigned to the estimating procedures used here supports the conclusion that implementing one of the lower cost treatment alternatives would result in significant savings compared with implementing the baseline carbon tetrachloride treatment system.

All of the treatment costs estimated for the alternatives are based on EUACs, and all of the cost effective alternatives compare favorably with the baseline treatment cost of \$5.68/lb noted above. In addition, all of these viable alternative technologies meet the process, logistical, and regulatory requirements mentioned above.

It was concluded from this evaluation that a treatment system utilizing condensation by liquid nitrogen is the most cost-effective alternative for 30,000 and 10,000 ppm_v carbon tetrachloride soil vapor concentration at an estimated cost of \$1.25 to 1.65/lb of carbon tetrachloride removed. Within this range, onsite use would be 15% less costly than offsite disposal. The cost for outlet concentration to polishing or standby GAC at either 10 or 100 ppm_v (-134 or -103 °F) differs by less than 3%. On the same basis, the estimated costs for mechanical refrigeration and thermal oxidation range from \$1.69 to 3.41/lb of carbon tetrachloride removed. The most cost-effective alternatives for 1,000 ppm_v carbon tetrachloride soil vapor concentration are three stage mechanical refrigeration at \$2.67/lb with use onsite and thermal oxidation at \$2.54/lb with offsite waste disposal. Three-stage mechanical refrigeration would have dual heat exchangers so half would be condensing and half would be defrosting. Thermal oxidation would have receiving, storage, baghouse, and handling for dry scrubbing trona powder and waste sodium chloride and excess trona.

The treatment cost for every alternative system is estimated to be less than that of the baseline system at 30,000 and 10,000 ppm_v. Treatment cost for mechanical refrigeration and liquid nitrogen are greater than the baseline treatment cost for those configurations listed in Table G-4 where the soil vapor carbon tetrachloride concentration is greater than or equal to the outlet concentration to the standby GAC. For these alternative configura-

tions, all of the equipment is idle but the investment would have been made and GAC would have to be used at the baseline rate. Treatment costs for the other, less expensive alternatives range from 45% of baseline for thermal oxidation at 1,000 ppm_v to 56% of baseline for two-stage mechanical refrigeration at 10,000 ppm_v.

Waste disposal cost was estimated to be on the order of 20% to 30% of annual cost for the most cost effective alternatives noted above. Offsite liquid waste disposal by incineration was estimated to be slightly more costly than onsite use. No cost was estimated for engineering or laboratory sample analysis to meet the onsite use acceptance criteria. Onsite use cost was based on the labor cost of one full-time operator and the assumed availability of an existing tank truck at no cost.

G.8.0 REFERENCES

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