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A. J. Schmidt
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September 1996

Prepared for
the U.S. Environmental Protection Agency
National Risk Management Research Laboratory
under U.S. Department of Energy
Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
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Summary

The overall objective of this project was to demonstrate an efficient, cost-effective means for remediating PCB-contaminated materials associated with U.S. Navy vessels. Towards this goal, the Base Catalyzed Decomposition technology was applied to the dechlorination of two types of PCB-contaminated materials generated from Navy vessel decommissioning activities at Puget Sound Naval Shipyard (PSNSY). These materials included insulation consisting of wool felt impregnated with PCB, and PCB-containing paint chips/debris from removal of paint from metal surfaces. The testing conducted under this project built upon the results from the BCD demonstration conducted by Pacific Northwest National Laboratory (PNNL) and Battelle-Columbus Laboratory (BCL) and the Navy for the treatment of contaminated soils and process residuals at the Navy Public Works Center in Guam.

The BCD process is a two-stage low-temperature chemical dehalogenation process that converts PCBs, pesticides, dioxins, furans, and other chlorinated compounds into nonhazardous materials. In Stage 1 of the process, which is typically applied to contaminated soils, materials containing halogenated contaminants are mixed with sodium bicarbonate and heated to approximately 350°C to vaporize and partially decompose the contaminants. The volatilized halogenated contaminants (e.g., PCBs, dioxins, furans), which are collected in a small volume of particulates and granular activated carbon (from water treatment), are decomposed by the liquid-phase reaction (Stage 2) in a stirred-tank reactor (STR), using a high-boiling-point hydrocarbon oil as the reaction medium, with addition of a hydrogen donor, a base (NaOH), and a catalyst. For treatment of PCB-containing materials from Navy vessel decommissioning activities, Stage 2 of the BCD process was the primary focus of this project. Some Stage 1 testing was also conducted.

The project was divided into two primary activities: 1) bench-scale screening studies and 2) pilot-scale testing. Bench-scale testing was conducted in a 2-L STR to provide information on the process chemistry and system operability specific to Navy vessel materials. Parameters investigated included BCD reagent dosages, temperature, reaction time, reaction media, and alternative chemical additions. The results of this treatability testing were then integrated into the 20-gal pilot-scale STR design. The purpose of the testing in the 20-gal STR was to confirm the laboratory-scale results in a near-production size system and to examine large-scale system operability.

The tests conducted for this evaluation showed that treating wool felt insulation and paint chip wastes with the liquid-phase BCD process (Stage 2) on a large scale is feasible. However, compared with current disposal costs for PCB-contaminated materials, using Stage 2 would not be economical at this time. For paint chips generated from shot/sand blasting, the solid-phase BCD process (Stage 1) should be considered, if paint removal activities are accelerated in the future.

Bench-scale Treatability Testing

The 2-L STR system consisted of a stainless steel reactor, an offgas/condensate system that included a moisture test receiver (MTR), a condenser, and a carbon bed for offgas cleaning. The operational setup is similar to the liquid phase reactors used during the BCD demonstration in Guam.

Once the required permits were obtained and shakedown testing conducted, baseline screening tests were initiated. The primary objectives for initial BCD testing included developing and demonstrating a reproducible, successful baseline recipe on the wool felt matrix. This baseline was a benchmark to compare the effects of major matrix changes in the BCD reagents, feedstock, or medium and also provide an acceptable starting point from which preliminary optimization could be performed. This recipe provided for a reaction slurry with an acceptable amount of solids in the reactor for ease of operations (about 26% by weight solids before dissolution).

Baseline BCD runs were conducted with wool felt at the temperatures and reagent loadings determined to be effective during the shakedown testing. For these tests, wool felt made up approximately 13% of the mass of the reactor contents; the mass ratio of NaOH to PCB was 6.25:1; and the ratio of reaction oil (LW-110) to wool felt was about 6:1. After a successful baseline run was conducted in which the PCB concentration was reduced from about 16,000 ppm to below the Toxic Substances Control Act (TSCA) target treatment level (i.e., less than 2 ppm per congener), the effects of catalyst and hydrogen donor oil (LW-104) were tested by omitting them from the feed matrix. A duplicate run of the baseline case was conducted to examine the repeatability of both the analytical results and the operability of the system.

Results from the baseline testing showed that, for the wool felt matrix, neither hydrogen donor oil (LW-104) nor catalyst are necessary and do not have a perceptible effect on the rate or extent of PCB destruction for treatment of wool felt. These tests also showed that operation and analytical results were repeatable from run to run.

A proprietary reagent developed by Battelle staff (at BCL and PNNL) was also tested in the bench-scale STR. Testing with the new reagent indicated that significant PCB destruction occurs at much lower temperatures than the baseline BCD process, reducing the nominal operating temperature from 350°C to 275°C. Lower operating temperatures would provide such benefits as lower costs, increased safety, reduced volatilization of PCB, reduced process time, and less energy output. Using the Battelle reagent allowed LW-104 to be substituted for LW-110 as the primary reaction medium, which yielded better separation between the solids and the oil phase at the conclusion of a test and ensured that the reaction medium could act as the hydrogen donor.

Tests with higher wool felt loadings than used in baseline runs were also performed because operation at higher waste loadings are desirable to enhance the process economics, since the waste loading determines the process throughput for a given reactor size. Wool felt loadings 2 (2X) and 3 (3X) times the baseline loadings were used. During the high loading tests, it was shown that, with wool felt containing approximately 14% by weight PCB, the reagent loading (relative to the baseline runs) could be reduced by 33%. Further testing indicated that at 50% of the baseline loadings, complete dechlorination of the PCB was not achieved. Furthermore, for the high wool felt runs discussed here, a much more aggressive approach was necessary to remove the treated material, since solids adhered to the sides and bottom of the reactor.

A number of screening tests were conducted with the paint chip waste form collected from shot blasting and other paint removal operations associated with decommissioning activities. Analytical results showed that the paint chips used for the screening tests contain between 500 and 600 ppm PCB. That is, each kilogram of paint chips contains only about 0.6 g PCB. Despite the relatively low PCB concentration, the disposal cost for paint chips approaches that of wool felt. Results from testing with paint chips showed that very high waste loadings were achievable, and that the treated product can be readily removed from the reactor. The treated product is a thick, homogeneous slurry, with little or no separable oil (i.e., little or no oil can be recycled for use in subsequent runs). Although the PCB concentration in the paint chips is low, to effect adequate treatment, NaOH must be added at a ratio approximately 100 times greater than the standard BCD NaOH:PCB mass ratio of 2.5:1. This indicates that much of the NaOH may be tied up or consumed by the paint chip matrix.

Other screening tests were conducted to examine BCD processing alternatives. A closed-system hydrothermal BCD run was conducted with no donor and no catalyst to examine the efficacy of using water as the reaction medium. After completion of the run, approximately 90% to 95% of the contents clarified. The analytical results showed that the PCB concentration was reduced from approximately 18,000 ppm to about 150 ppm after 2 hr at 350°C.

Paint chip waste associated with shot/sand blasting contains metal fines, spent blasting sand, wood, plastic, and other miscellaneous debris. Because of the high inorganic solids content, the material was tested for treatment via Stage 1 of the BCD process. Three conditions were evaluated: 1) Stage 1 with no sodium bicarbonate (i.e., unassisted thermal desorption; 2) Stage 1 baseline (i.e., paint chips to which 10% by weight sodium bicarbonate had been added; and 3) Stage 1 with a desorption additive. The paint chips were heated to 350°C and held there for 1 hr. A nitrogen purge was maintained over the reactor to sweep the system and to ensure the exclusion of air. Analytical results showed that the PCB concentrations for all three conditions were reduced from approximately 260 ppm to less than 2 ppm total. These results indicate that BCD Stage 1 and unassisted thermal desorption are potentially viable methods for the treatment of the paint chips/debris from PSNSY.

Pilot-scale Testing

The pilot-scale STR consisted of a 20-gal, 304 stainless steel reactor designed to operate up to 400°C at up to 5 psig. The STR was sized to treat approximately 12 gal (45 L) of material per batch (i.e., reactor contents to occupy about 60% of total volume). As a safety precaution, there were no penetrations in the walls or bottom of the STR. Heat was supplied to the reactor with four 2-piece mica band heaters. Agitation was provided with a gear-driven, flange-mounted, propeller-type mixer. The propeller was sized at 1/3 the tank diameter. A spiral plate heat exchanger with 3.78 ft^2 of heat transfer area was installed in a downflow configuration to condense organic and water vapors in the offgas. Condensed steam and oil flowed into the condensate receiver and did not reflux back into the reactor. The exit gas from the condensate receiver tank was polished in an granular activated carbon (GAC) filter before being vented.

Three pilot-scale runs were conducted using wool felt as the PCB-containing feedstock, and a fourth run was conducted using a 50/50 mix of wool felt and paint chips as the feedstock. The first two pilot-scale tests with wool felt did not adequately the PCB. In both of these runs, PCB was reduced from approximately 75,000 ppm to about 10,000 ppm. After completing these runs, it was determined that the PCB content in the wool felt was approximately 33% by weight, which is more than twice the content of the wool felt used during the bench-scale runs. Consequently, for these two runs, the quantity of NaOH added to the reactor was insufficient. For the third run, the unsuccessfully treated product from the second run was re-treated with additional NaOH. In that run, analytical results showed that near-complete destruction was achieved as early as 1 hr at 275°C. In the fourth run, approximately 500 ppm PCB remained after 2 hr at 275°C. The temperature was increased to 300°C and 325°C and held at both temperatures for 1 hr. At 300°C, the PCB concentration was reduced to about 100 ppm, and was further reduced to less than 10 ppm total after 1 hr at 325°C.

Operationally, all pilot-scale runs were highly successful. During the first run, an aggressive heating strategy was pursued, and no boilovers or foaming events occurred. Operations at the hold temperatures were uneventful for all runs.

The noncondensible offgas exiting the system (downstream of the GAC bed) exhibited a distinct ammonia odor. Additionally, the quantity of noncondensible offgas was significantly higher than anticipated. Each liter of material in the reactor generated approximately 6 to 8 L of offgas. Analyses of the offgas showed that approximately 90% was hydrogen, and about 6% was methane.

The reactor contents were pumped out by pressurizing the reactor to approximately 110 mm Hg, and opening the pump-out line, which was connected to a dip leg that extended to the bottom of the reactor. With this method, it was possible to safely empty the reactor at temperatures near 200°C. However, large quantities of solids were left in the reactor. After the first run, the product was allowed to settle, and approximately 70% of the oil initially charged to the reactor was recovered (including collected organic condensate) and reused in the next run.

While the first two runs generated between 2 and 3 kg of organic condensate, the third run (to which additional reagent had been added) generated nearly 8 kg. With so much of the oil removed from the reactor, pumping out solids proved problematic. After pumping, a 12-kg heel of hardened solids was left in the reactor. During the fourth run, in which a higher boiling oil (LW-110) was used as the reaction medium, only 0.6 L of organic condensate was generated. After the run, about 96% of the oil added to the reactor was recovered (including approximately 0.5 kg of organic condensate) for potential reuse in subsequent runs. Despite using a higher oil:wool felt ratio, solids accumulation in the reactor was again a problem. Removal of the solids (approximately 15 kg) required the use of a hammer and chisel.

Conclusions from the pilot-scale testing can be summarized as follows: 1) Treatment of PCB in wool felt and paint chips is feasible in a large-scale system. 2) Removal of the treated product can be enhanced by avoiding bottom and side cooling of the reactor (i.e., this type of cooling resulted in a portion of the reactor contents "freezing" along the walls and bottom of the reactor. 3) A substantial fraction of the reaction oil may be recycled for subsequent runs. 4) Use of higher-boiling-point oil (i.e., LW-110) significantly reduces the quantity of organic condensates generated. 5) Removal of solids is problematic with the waste tested and will need to be addressed in the design of a full-scale system.

Economics of a Full-scale System

The economics of the liquid-phase BCD process were evaluated in terms of capital and operating costs for a 300-gal batch system for treatment of a feedstock of 91 kg each of wool felt and paint chips/debris in each batch. For this analysis, the following assumptions have been made: 1) The system will process one batch per day. 2) The system will run 5 days per week, 50 weeks per year. 3) Capital costs were depreciated over 10 years to obtain a total annual operating cost and the unit cost ($/kg) for the treated wool felt and paint chips.

The total purchased equipment cost for the STR system was estimated to be $110K in May 1996 dollars, using the Chemical Engineering Plant Cost Index. In addition to the purchased equipment costs, the fixed capital investment (FCI), which includes other direct and indirect costs (e.g., installation, piping, electrical, site preparation, etc.), was estimated to be $310K to purchase and deploy a 300-gal BCD STR system. The total annual treatment cost, which includes both FCI depreciation and operating costs is projected to be $540K/year for the 300-gal BCD system with a 10-year life. The unit cost for treating 45,500 kg per year of wool felt and paint chips is estimated at $11.90/kg. Approximately 40% of the total treatment costs are from chemical reagents and the disposal of the treated material. Without an extensive and expensive sampling program, it is unlikely that the chemical costs can be reduced substantially.

Current disposal costs for wool felt and paint chips generated from PSNSY vessel decommissioning activities range from approximately $4/kg to $6/kg. Consequently, use of Stage 2 BCD for treatment of these streams does not appear to be economical. Stage 1 tests with paint chips generated from shot/sand blasting activities showed that Stage 1, with and without the sodium bicarbonate catalyst, removed the PCB in the paint chips to below the TSCA treatment target.

A recent evaluation performed for the Guam demonstration examined the economics of BCD Stage 1 and Stage 2 combined to treat PCB-contaminated soils. This evaluation gave a total treatment cost of $400/metric ton ($0.40/kg) for a system processing 7000 metric tons per year. Consequently, if paint removal activities at PSNSY are heightened, and the quantity of paint chips generated increases substantially (over the 20,500 kg/yr currently projected), use of BCD Stage 1 may be a suitable alternative treat this stream.

Acknowledgments

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The authors gratefully acknowledge the U.S. Navy coordinator for this project, Dr. DB Chan (Naval Facilities Engineering Service Center), and Chris Williams (Puget Sound Naval Shipyard, Code 250.33), who served as the point of contact for PSNSY.

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Abbreviations

APEG	Alkali metal polyethylene glycols
BCD	Base Catalyzed Decomposition
BCL	Battelle-Columbia Laboratory
CB	Chlorobiphenyl
CBD	Commerce Business Daily
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
DCMA	Dry Cleaning Manufacturer's Association
ECD	electron capture detector
EPA	U.S. Environmental Protection Agency
FCI	fixed capital investment
GAC	granular activated carbon
GC/MS	gas chromatograph/mass spectrometer
KPEG	potassium polyethylene glycol
LCS	laboratory control standard
MTR	moisture test receiver
NaPEG	sodium polyethylene glycol
NRMRL	EPA's National Risk Management Research Laboratory
OPPT	Office of Pollution Prevention and Toxics
PCB	polychlorinated biphenyls
PEG	polyethylene glycol
P&ID	piping and instrumentation diagram
PNNL	Pacific Northwest National Laboratory
PSNSY	Puget Sound Naval Shipyard
PWC	Public Works Center
QAPP	Quality Assurance Project Plan
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RD&D	research, development, and demonstration
RPD	relative percent difference
RREL	EPA's Risk Reduction Engineering Laboratory
SARA	Superfund Amendments and Reauthorization Act
SERDP	U.S. Department of Defense Strategic Environmental Research and Development Program
SSA	sources sought anouncement
STR	stirred-tank reactor
TDC	total direct costs
TIC	total indirect costs
TSCA	Toxic Substances Control Act

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1.0 Introduction

The overall objective of the work described in this report was to demonstrate an efficient, cost-effective means for remediating polychlorinated biphenyl (PCB)-contaminated materials associated with U.S. Navy vessel recycling activities. In the past, PCBs were added to the insulation used in Navy vessels to increase fire resistance and for other reasons. PCB compounds were once widely used for many industrial applications; however, in time, the safety of PCBs became a concern (Hutzinger and Veerkemp 1981; Hutzinger et al. 1974), and they were ultimately banned from further use (Erickson 1992). Because of the toxic and carcinogenic nature of these compounds, and as a result of environmental statutes and laws, the Navy is seeking methods and processes for treating PCBs. The project discussed here was conducted with materials from the Puget Sound Naval Shipyard (PSNSY) in Bremerton, Washington, where work is under way to decommission and dismantle retired vessels, which includes removing insulation and other components containing PCBs.

The Navy is required by the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), the Superfund Amendments and Reauthorization Act (SARA), and the Resource Conservation and Recovery Act (RCRA) to clean up hazardous substances to minimize the amount of hazardous wastes that are produced. These laws further provide for research, development, and demonstration (RD&D) of methods to clean up and reduce the toxicity of hazardous substances in the environment.

This report discusses the application of the Base Catalyzed Decomposition (BCD) technology on PCB-containing materials from PSNSY. This process was successfully demonstrated for PCB cleanup at the Navy's Public Works Center (PWC) on Guam (Schmidt et al. 1996). The development and scaleup of the BCD process was a joint effort conducted by the U.S. Environmental Protection Agency (EPA), the Navy, Pacific Northwest National Laboratory (PNNL),(a) and Battelle-Columbus Laboratory (BCL). A 1 to 2 ton per hour continuous system was designed and built by engineers at PNNL and BCL from a laboratory process developed by EPA's Risk Reduction Engineering Laboratory (RREL) (Schmidt et al. 1996). The full-scale system was designed and deployed at the PWC on Guam by PNNL and transferred to the Navy's remedial action contractor in November 1994.

The BCD technology is a low-temperature chemical dehalogenation process that converts PCBs, pesticides, dioxins, furans, and other chlorinated compounds into nonhazardous materials. For treating the PCB-contaminated materials from Navy vessels, a slurry consisting of a bulk reaction medium, BCD reagents, and the PCB-contaminated materials is fed to a stirred-tank reactor (STR), where it is heated and held at the target operating temperature. During the process, the PCBs are decomposed and the reactor contents are removed.

(a) Operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Bench-scale treatability tests were performed to determine the operating conditions specific to the wastes involved and to more thoroughly investigate the process chemistry. Parameters investigated included reagent makeup and concentration, temperature, and reaction time. From the results of the bench-scale tests, a pilot-scale reactor was designed and procured for demonstration testing. The pilot-scale system was used to process two PCB-containing waste forms from PSNSY: wool felt insulation and paint chips. These materials are uncommon feedstocks for PCB treatment processes. Common feedstocks for PCB treatment include soil and other environmental media contaminated through past disposal practices or leaks.

This project was a cooperative program involving participation by PNNL, EPA's National Risk Management Research Laboratory (NRMRL), and the U.S. Navy. The program was funded by the EPA-NRMRL through the U.S. Department of Defense's Strategic Environmental Research and Development Program (SERDP).

In-depth project documentation was required before testing could be performed with PCB-containing wastes. In October 1994, a Research and Development (R&D) permit application under the Toxic Substances Control Act (TSCA) was prepared and submitted for review. The EPA Office of Pollution Prevention and Toxics (OPPT) granted PNNL an R&D Permit on July 13, 1995. This permit allowed PNNL to conduct BCD testing on up to 1100 lb of wool felt, plastic unicellular material, and painted metal and paint chips for a period of 1 year.

On July 22, 1996, EPA-OPPT granted PNNL a renewal and amendment to the R&D permit to conduct further testing on the disposal of PCB. The new permit applies to BCD and KPEG (potassium ethylene glycol) technologies and to the testing and evaluation of a wide variety of paint removal technologies for painted metal containing PCB.

In addition to the R&D permit, EPA-NRMRL required that PNNL submit and obtain approval of a Quality Assurance Project Plan (QAPP) before testing was initiated. The QAPP was endorsed by the NRMRL Quality Assurance Department in October 1995.

Other necessary project documentation that has been completed and approved included a test plan (approved by EPA-NRMRL in August 1995); a waste management plan (February 1995); and three safe operating procedures for test system operations.

Once the R&D permit was received, shakedown testing was performed to develop protocols and testing strategies, and refine sampling and analytical procedures to finalize the QAPP. During July and August 1995, four shakedown runs were completed. Upon approval of the QAPP in October 1995, the bench-scale tests were initiated. Between October 1995 and August 1996, 21 tests were conducted in which more than 30 conditions were examined. From June to August 1996, four tests were run with the pilot-scale system. The results of the bench-scale and pilot-scale tests are discussed here.

This report also gives a brief history of the process development, and describes the bench-scale and pilot-scale systems, the waste materials being treated, and the analytical methods used. An economic assessment for a full-scale system is also provided. The appendices contain analytical data, and more detailed information on analytical procedures, quality assurance, and the basis for the scaled-up economics.

2.0 Process History and Development

This section reviews the BCD process chemistry and the application of the process for treatment of PCB-contaminated soils and residuals at the PWC in Guam and the scaleup for demonstration and deployment on Guam (Schmidt et al. 1996); then summarizes applications for treating PCB-contaminated materials associated with Navy vessel recycling activities.

2.1 Chemistry and Evolution

The development of a dehalogenation process began in 1978 when the Franklin Research Center synthesized a new chemical reagent for the destruction of PCB (EPA 1992). Eventually, a group of reagents generically referred to as "APEGs" (alkali metal polyethylene glycolates) were developed (EPA 1989, 1990). These reagents were based on the reaction of alkali metals [such as sodium (Na) or potassium (K)] or their hydroxides with polyethylene glycols (PEG) or their derivatives, as shown in Reaction (1).

$$\text{R-Cl}_x + \text{A-PEG} \xrightarrow{\Delta H} \text{R-(Cl)}_y\text{-OR}' + \text{ACL} + \text{R-(Cl)}_y\text{-OH} \qquad (1)$$

The reagents prepared by reacting sodium (or potassium) hydroxide and polyethylene glycol were known as NaPEG (or KPEG). Proposed mechanisms for dechlorination with APEGs involved nucleophilic substitution and oxidative dehalogenation of organic compounds under mild conditions (75°C to 120°C). Hydroxide and alkoxide ions displace halides of halogenated aromatics to yield phenols and aromatic ethers, respectively. One disadvantage of the APEG process was that increased moisture content in the material being treated reduced its effectiveness and increased reagent consumption. Also, the reaction byproducts remained in the treated waste matrix, and their long-term stability was not known.

In July 1987, pilot-scale testing of the APEG process was conducted by EPA with a 40-gal reactor at Moreau, New York (Taylor et al. 1989). During the testing, PCB-contaminated soil (140 to 7000 ppm - averaging 1990 ppm PCB) was treated in four batches, each weighing approximately 16 kg. The PCB concentration in the treated product ranged from 1.1 to 12.4 ppm and averaged 5.6 ppm, yielding an overall destruction rate of greater than 99%. This testing demonstrated the feasibility of the APEG process and provided the data used to design a larger pilot-scale reactor for subsequent testing by the EPA and the Navy in Guam.

In April and October 1988, a 400-gal Littleford mixer (modified as a batch APEG reactor) was field-tested on 27 tons of soil at PWC-Guam with soil containing 2500 to 4500 (averaging 3430) ppm PCB. Eight runs with approximately 1700 kg of soil each were conducted in which the soil and reagents were heated to 150°C, held there for 4 hr, and then allowed to cool overnight. For each ton of soil treated, approximately 410 kg of polyethylene glycol (PEG-400) and 77 kg of potassium hydroxide were added. After cooldown of the reactor contents, approximately 73 kg of sulfuric acid (H_2SO_4) per ton of soil were added to neutralize the soil for pH adjustment to the 7-9 range as specified in the TSCA RD&D Permit. The treatment resulted in a PCB reduction of greater than 99%; however, in four of the runs, a tetrachlorobiphenyl congener concentration in the treated matrix was slightly above the 2 ppm per congener treatment criterion specified in the permit. Batches not meeting the 2 ppm per congener criterion were reloaded into the reactor with fresh reagent and successfully re-treated to meet the permit standard.

An evaluation of data from APEG treatment of soil in Guam showed that additional research and process development were needed if halo-organic contaminated sites were to be remediated by dehalogenation technology. The following improvements were identified as essential, and criteria were established for a new dehalogenation technology (Rogers et al. 1991a; Rogers 1994):

- Eliminate the need for reagent recovery.
- Utilize low-cost reagents (i.e., base, catalyst, hydrogen donor, reaction medium) in the treatment process.
- Develop continuous processing capabilities.
- Reduce process treatment time from the 4 to 6 hr required by the APEG process.
- Destroy or remove nonhalogenated pollutants from contaminated matrices.
- Completely dehalogenate pollutants with high and low degrees of halogenation.
- Pollutants in treated matrices must be destroyed to regulatory compliance where residues can be disposed of onsite.

Based on the conclusions from the APEG testing, investigations of catalytic transfer hydrogenation were conducted in which organic materials were used as hydrogen donors in the presence of a catalyst for dehalogenating organic contaminants. The catalytic transfer hydrogenation reaction is generalized in Reaction (2).

$$\text{Donor-H} + \text{Acceptor} \xrightarrow[> 300^\circ\text{C}]{\text{base catalyst}} \text{Donor} + \text{Acceptor-H} \qquad (2)$$

In 1989, experimental laboratory data confirmed a chemical reaction involving the hydrogen transfer for the removal of halogens from a variety of compounds (Rogers et al. 1991a; Rogers 1994), and in 1991 three U.S. Patents (5,019,175; 5,039,350; 5,064,526) were awarded to EPA (Rogers et al. 1991b-d). From this work, the eventual two-stage BCD process evolved (EPA 1991). BCD Group, Inc., a company formed by the process developers, continued to work on enhancements to this process.

Figure 2.1 illustrates the major steps in the process. In Stage 1, materials containing halogenated contaminants are mixed with sodium bicarbonate and heated to approximately 350°C to vaporize and partially decompose PCBs or other halogenated contaminants. The volatilized halogenated contaminants (e.g., PCBs, dioxins, furans), which are collected in a small volume of particulates and granular activated carbon (GAC) (from water treatment), are decomposed by the liquid-phase reaction (Stage 2) in the stirred-tank (slurry) reactor (STR), using a high-boiling-point hydrocarbon oil medium, with addition of a hydrogen donor; a base, sodium hydroxide (NaOH); and a catalyst. For treatment of PCB-containing materials from Navy vessel decommissioning activities, Stage 2 of the BCD process was the primary focus.

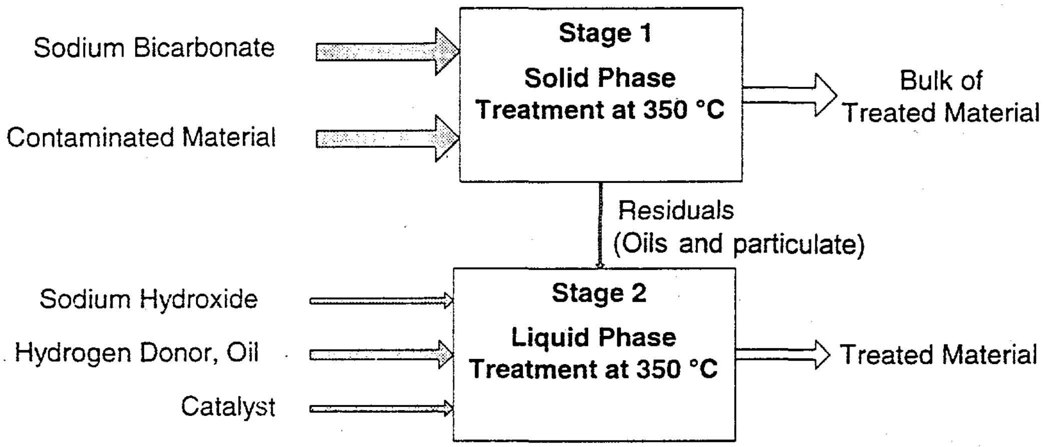
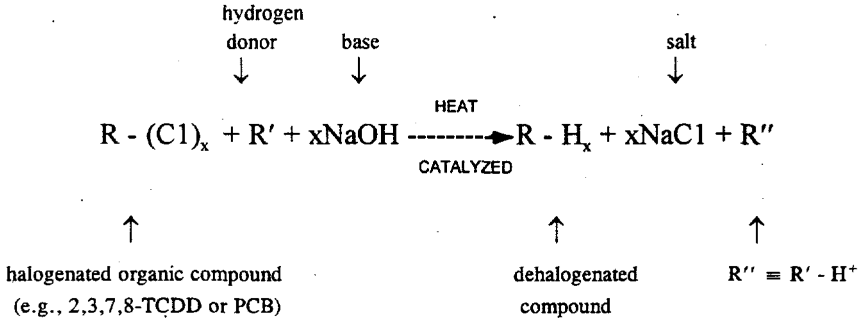


Figure 2.1. Major Steps in the BCD Process, Solid and Liquid Phases

The base-catalyzed dechlorination reaction conceptualized is illustrated in Reaction (3). This dehalogenation reaction, which occurs in Stage 2, is also expected to take place to some degree in Stage 1 if there is a natural hydrogen donor in the waste matrix.



$$\underset{\substack{\uparrow\\ \text{halogenated organic compound}\\ \text{(e.g., 2,3,7,8-TCDD or PCB)}}}{R - (Cl)_x} + \overset{\substack{\text{hydrogen}\\ \text{donor}\\ \downarrow}}{R'} + \overset{\substack{\text{base}\\ \downarrow}}{xNaOH} \xrightarrow[\text{CATALYZED}]{\text{HEAT}} \underset{\substack{\uparrow\\ \text{dehalogenated}\\ \text{compound}}}{R - H_x} + \overset{\substack{\text{salt}\\ \downarrow}}{xNaCl} + \underset{\substack{\uparrow\\ R'' \equiv R' - H^+}}{R''} \qquad (3)$$

2.2 Process Design Testing and Scaleup

Laboratory experiments on both the solid-phase and liquid-phase reactions were conducted by BCL and EPA-RREL to provide design data for the scaleup of the BCD process for deployment in Guam.

Based on the results of the laboratory testing, PNNL and BCL assisted the Navy in designing and building a 1 to 2 ton per hour continuous treatment system. The completed system is Navy-owned and was assembled and cold tested at a Navy site in Stockton, California, prior to shipment to Guam. The system was shipped to Guam in August 1992, cold tested there in June and July 1993, successfully tested with 16 tons of PCB-contaminated soil in January 1994, and again with 50 tons in November 1994. In May 1995, the liquid portion of the BCD system (Stage 2) was successfully demonstrated in a 400-gal STR. After the November 1994 testing, BCD operations were transferred to the Navy's remedial action contractor for deployment at the Guam site.

The BCD process was carried out in two steps following excavation and feed preparation: 1) a solid-phase reaction using an indirectly heated rotary reactor (Stage 1), and 2) a liquid-phase reaction using an STR (Stage 2). The solid process used a base (sodium bicarbonate) and an organic source of hydrogen to partially decompose and volatilize PCBs in the soil at 350°C for 1 hr. Offgas from the primary rotary reactor was cleaned by a cyclone, baghouse, venturi scrubber, and GAC to remove PCBs prior to venting. PCBs recovered from the offgas treatment system were treated in the liquid-phase STR utilizing a base (NaOH), an aliphatic hydrocarbon solvent, and a catalyst at 350°C for 1 to 2 hr. Treated soil has been demonstrated to meet the treatment criterion of less than 2 ppm per resolvable PCB congener. Note: for PCBs, there are 209 distinct congeners/isomers that are identified both by degree of chlorination (i.e., number of chlorine atoms on the specific PCB) and by the positions of chlorine atoms on the biphenyl rings (also see Section 3.2).

All systems (except for the reactor, crushing plant, and mixing plant) were modular and skid-mounted for placement in a 40-ft overseas shipping container. A complete analytical laboratory (gas chromatograph/mass spectrometer, GC/MS) and a shop were also built into containers used in Guam.

2.3 BCD Process Design and Chemistry as Applied to Waste Forms from PSNSY

For application of the BCD process to PCB-containing wastes from PSNSY, testing efforts focused on Stage 2 of the process. The selection to evaluate Stage 2 was made primarily as a result of the makeup of the two waste streams evaluated: wool felt and paint chips. Wool felt, used mainly as an insulation and gasketing material, consists of wool fibers impregnated with Aroclor 1268 (trademark of Monsanto Corporation) a mix of highly chlorinated PCBs. Painted surfaces on Navy vessels became contaminated with PCB from contact with wool felt and also from direct addition of PCBs into high-temperature-resistant paint formulations. These matrices are described in more detail in Section 3.1.

Stage 1 is generally applicable to a waste stream containing relatively low PCB concentrations (i.e, typically less than several percent PCB) and low organic content. Furthermore, Stage 1 does not effect complete treatment of PCBs (i.e., Stage 1 is a combination of destruction and thermal desorption). Therefore, for a waste stream such as wool felt, which is primarily organic and contains a very high PCB concentration, BCD treatment via Stage 2 is the most appropriate treatment methodology.

Some paint chips originate from shot blasting during paint removal work. However, other paint chips result from paint removal with needle guns and scrapers. The paint chips that do not contain shot blast are also more appropriately treated in Stage 2. Although the PCB concentration is typically less than 1000 ppm, a significant fraction of the matrix is organic. Approximately 25% of the mass was removed by heating to 350°C and holding to 1 hr.

Paint chips from shot blasting contain a significant quantity of metal fines and spent shot blast. When this material was heated to 350°C (and held for 1 hr), only 7% of the mass was removed. Consequently, the paint chips collected in the cyclone from shot blasting present an appropriate stream for consideration of treatment via Stage 1.

The investigation of the BCD process as applied to the wool felt matrix has provided insight into the likely mechanisms for the dechlorination reactions. The postulated two semi-independent mechanisms are described here. As noted previously, the PCB makeup in wool felt is primarily Aroclor 1268, which has an average of 8.7 chlorine atoms per molecule of PCB. In comparison, a relatively common Aroclor, 1254, has an average of 5 chlorines per PCB molecule. The highly chlorinated makeup of Aroclor 1268 contributes to the apparent two-mechanism dechlorination pathway.

The first mechanism, primarily responsible for the initial dechlorination of highly chlorinated biphenyls, is most likely an electrophilic substitution reaction. It is driven as much autocatalytically by the chlorines at specific ring relationships as catalytically by the available NaOH. This mechanism is probably responsible for chlorine reduction from 10-chlorobiphenyl (10-CB) to 6-CB homologs. Note: for PCBs, homologs (also see Section 3.2) refer to the degree of chlorination (i.e., monochlorinated, dichlorinated, trichlorinated, etc.). This mechanism is fast and occurs at relatively low temperatures (i.e., < 300°C). During testing with wool felt, nearly all of the 10-CB to 7-CB reduced to 6-CB and lower during reactor heatup and before the target reaction temperatures were achieved.

After the faster reaction eliminates some of the chlorines (and thus much of the Cl-Cl interaction ring position interaction), the slower second mechanism emerges, which may be a form of the *elimination-addition mechanism* called the *benzyne* (or in this case, potentially *phenol-benzyne*) *mechanism*. This second mechanism is responsible for the elimination of the remaining chlorines (6-CB and below).

The second mechanism requires the intimate presence of a strong base, in this case NaOH, and occurs at higher temperatures (i.e., 275°C to 350°C). For example purposes, a chlorine at Position 4 and a hydrogen at Position 3 will be considered (Figure 2.2). [Note, the actual relative kinetics among the various available attached chlorines and hydrogens were not investigated.] In the strongly basic environment, the first step occurs when the proton at Position 3 is abstracted by the available hydroxide ion. This step generates water and a carbanion in the primary ring, as the bare proton is stripped away leaving the electron pair on the carbon ring (a Lewis base).

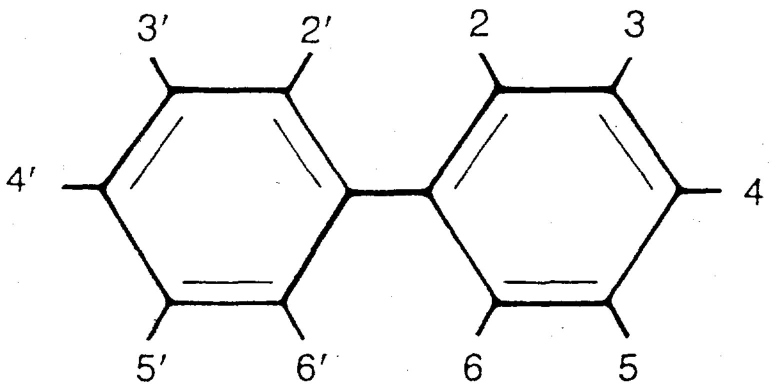


Figure 2.2. Structure of a Polychlorinated Biphenyl Molecule

The elimination is the second step of this reaction in which the chlorine at Position 4 on the ring dissociates from the ring as Cl^- while the carbanion at Position 3 forms another partially stable bond with the fourth carbon, forming a temporary chlorinated phenyl-benzyne. This phenyl-benzyne molecule may eventually strip off a loosely bound proton from an available "hydrogen donor" in the reaction matrix, which may be long-chain nonpolar hydrocarbons (e.g., LW-104 oil) or other decomposable hydrogen donors such as wool felt. This process is repeated until all chlorine atoms are removed from the biphenyl molecule.

The rehydrogenation of the chlorinated phenyl-benzyne molecule may take a slightly different pathway. Rather than stripping protons from an available hydrogen donor, the phenyl-benzyne molecule may, under certain circumstances, polymerize with another chlorinated biphenyl, the hydrogen donor, or other short-chain organics in the matrix.

This behavior may be observed in partially treated wool felt samples with the BCD process. Analysis of the samples indicated that as treatment progresses, a group of compounds are found that elute from the GC column much later than the 10-CB isomer, the last PCB to elute. The detected peaks are near Bernoullian in distribution and display the signature of a large grouping of very closely related compounds, presumably what would be formed in the random polymerization of the partially chlorinated biphenyls.

This chlorinated "polymerized biphenyl" grouping, under further treatment, appears to slowly decay in total detected area, as well as eluting earlier off of the column. This, presumably, indicates that the chlorinated polymers are still being dechlorinated by the BCD mechanism (hence the shift to lower column residence time) and are being eliminated in population (shown by the reduction of area underneath the peaks on the chromatograms). The chlorinated polymer peaks in the samples analyzed decayed completely before the last of the 1-CB and 2-CB homologs, and are thus not considered an issue when processing a sample to complete destruction.

3.0 Description of Waste Matrices and Analytical Procedures Used

Polychlorinated biphenyls are a family of compounds produced commercially by direct chlorination of biphenyls using ferric chloride and/or iodine as the catalyst (Doull and Abrahamson 1986). PCBs were manufactured and sold as complex mixtures differing in their average chlorination level. The crude mixtures resulting from the chlorination were fractionally distilled to produce commercial mixtures with the desired properties. The products range from light oily fluids (di-, tri-, and tetrachlorobiphenyls) to heavy, honey-like oils (pentachlorobiphenyls), to greases and waxes (more highly chlorinated).

The most important physical properties of the mixtures are that they are liquids, have low vapor pressures, low water solubility, and excellent dielectric properties. Chemical properties include stability to oxidation, flame resistance, and relative inertness. Because of the excellent flammability, electrical, and stability properties, PCBs found application in a wide variety of industrial uses, including heat transfer fluids, hydraulic fluids, solvent extenders, plasticizers, flame retardants, organic diluents, and dielectric fluids (Doull and Abrahamson 1986). Also because of these properties, PCBs were used in a number of materials for the construction of Navy vessels.

3.1 Vessel Materials Containing PCBs

Descriptions and characteristics of the PCB-containing materials that were evaluated in this project are given below.

3.1.1 Wool Felt, Gasket Material (Impregnated) (MIL-G-20241)

For most of the testing conducted, wool felt was used as the source of PCB. Testing with wool felt in the 2-L STR indicated that the material begins to disintegrate around 100°C, and a mixable slurry results at temperatures between 120°C and 200°C (depending upon waste loading). Wool felt used for most of the bench-scale testing contained about 140,000 ppm PCB. The wool felt used in much of the pilot-scale testing contained 320,000 ppm PCB. Information obtained during extraction showed that approximately 30% of the wool felt matrix is extractable in a 90:10 hexane/acetone mixture. With wool felt, a high waste loading is achievable. Several tests have been successfully completed with wool felt comprising approximately 32% by weight of the reactor contents.

Provided below are descriptions of wool felt from the military specification documentation (MIL-G-20241):

- Used as gasket material for joints of nonwatertight and watertight ventilation ducts and as an insulating material between dissimilar metals. One side of gasket is coated with a thin film of pressure-sensitive adhesive.

- Carrier Material: must contain minimum of 75% wool fibers.

- Impregnating Compound (i.e., PCB): nondrying, nonoxidizing, anticorrosive, chromated compound. The impregnating compound to carrier ratio shall be not more than 4.5:1.

- Dimensions: 1/16, 1/8, and 1/4 in. thick weighing a maximum of 3, 5, and 10 lb/yd^2, respectively.

- Analysis: 350,000 ppm PCB is typical at PSNSY. Maximum concentration found to date = 750,000 ppm. Analyses indicated that the PCB in wool felt is Aroclor 1268.

3.1.2 Polyurethane, Plastic Unicellular Material (MIL-P-15280)

Testing with plastic unicellular foam insulation was originally planned as part of this project; however, no screening tests were conducted. In July 1995, physical characterization testing was conducted to examine the behavior of unicellular polyurethane in the reaction matrix. Even at temperatures up to 330°C the unicellular material did not dissolve. Since both the density of the unicellular material (0.048 to 0.13 g/cm^3) and average PCB concentration (100 ppm) are low, achieving a high waste loading in a reactor may not be possible. For example, if a 400-gal STR were loaded to capacity (without compressing the unicellular material), it would only contain about 20 g of PCB (using 100 ppm and density of 0.13 g/cm^3). If the unicellular material is compressed, it is likely that a mass transfer barrier will disrupt the BCD reaction.

The unicellular polyurethane insulation is described below from the military specification documentation (MIL-P-15280):

- Chemically expanded unicellular elastomeric plastic foam material for thermal insulation.

- Specification for this material does not indicate what types of polymers were used. However, the specification references a number of ASTM testing standards, including Standard Specification for Flexible Cellular Materials - Sponge or Expanded Rubber (D-1056); Standard Specification for Flexible Cellular Materials - Vinyl Chloride Polymers and Copolymers (Closed Cell Foam) (D-1667).

- Dimensions: Material was fabricated into sheets and tubes of various dimensions.

- Analysis: The specification does not call out PCB as a required constituent; however, recent analysis showed that the concentration of PCB falls around 50 to 100 ppm and 250 to 500 ppm. The concentration is rarely above 1000 ppm, and the maximum ever seen was about 10,000 ppm. Analyses indicate the PCB in foam insulation typically consists of Aroclors 1250 through 1260.

3.1.3 Paint Chips and Painted Metal

Paint chips containing PCBs were provided by PSNSY for use in screening tests. From a weight perspective, PCB-contaminated painted metal surfaces represent the largest PCB waste stream from vessel decommissioning activities. Some types of paint (e.g., heat-resistant aluminum paint) were originally formulated with PCB. Other painted surfaces were contaminated through contact with PCB-containing insulation material. Currently, large (heavy) pieces of metal are blasted with steel shot to remove PCB-containing paint. Small pieces of painted metal are typically disposed of in permitted landfills. As a part of this R&D activity, paint chips were subjected to BCD investigations. Typical paint types include heat-resistant aluminum paint, originally formulated with PCB (TT-P-28 and MIL-P-14276); hull paint, contaminated from contact with wool felt (MIL-P-24441); and habitability paint (MIL-P-244441).

- Typical analysis: 300 ppm PCB is typical for paint chips at PSNSY. Generally, the paint contains no smearable contamination (i.e., swipe tests are generally negative). Analyses of paint chips from shot blasting indicated that the PCB is typically composed of Aroclors 1254 through 1260.

3.2 Description of Analytical Procedures

Achieving the project objectives required cost-effective, relatively fast analytical methods with low detection limits. Accordingly, methods were developed from existing standard procedures to meet the project needs, including expedient extraction and cleanup methods tailored specifically to the samples generated; a halogen-sensitive gas chromatograph (GC) coupled with an electron capture detector (ECD); and a precise pseudo-congener identification/interpretation method.

Understanding the objectives of the analytical method and the interpretation of the data generated requires that the terms "congener" and "homolog" (also referred to in Section 2.0) as applied to PCB molecules be defined:

> **Congener**. For PCBs, there are 209 distinct congeners/isomers that are identified by both the degree of chlorination (i.e., number of chlorine atoms on the specific PCB) and by the positions of the chlorine atoms on the biphenyl rings. Examples of specific congeners are: 2-chlorobiphenyl (a monochlorinated biphenyl); 2,2,3,3,6,6-hexachlorobiphenyl. Not all of the individual congeners are completely resolvable on the GC/ECD with this particular program.
>
> **Homolog**. For PCBs, homologs refer to degree of chlorination (i.e., monochlorinated, dichlorinated, trichlorinated, etc. Examples of monochlorinated homologs are: 2-chlorobiphenyl, 2'-chlorobiphenyl, 3-chlorobiphenyl; often abbreviated as 1-CB, 2-CB, etc.

This section provides an overview of the procedures used for sample extraction and cleanup, quantification, interferences, and data interpretation. A more detailed description of the analytical quantification method and quality assurance measures is provided in Appendix A.

3.2.1 Extraction/Cleanup Procedures

Several methods were tested on various matrices that included a mid-weight oil matrix (treated and partially treated), an aqueous matrix, a GAC matrix, and a solid or slurry matrix. The methods tested were selected on the basis of acceptable recovery, minimization of total waste generation, speed and ease of operation, minimization of contaminated glassware, and minimization of adverse impact on GC operation.

3.2.1.1 Liquid (Oil)-phase Extraction

The primary matrix analyzed was the LW-110/LW-104 batch reactor medium containing various states of thermally and chemically degraded PCB and reagents. Standard cleanup procedures for oil matrices are well developed for the analysis of transformer and hydraulic oils; however, historically, these matrices have been determined to be more difficult to extract and analyze than other sample types. The procedures include bulk dilution, Florisil cleanup, and acid/permanganate liquid/liquid cleanup. Each of these procedures was evaluated, and a commercially available Florisil procedure was ultimately selected as the baseline sample cleanup method for the oil-phase samples.

Bulk solvent dilution, which was tested first, was found to be unacceptable, as it significantly raised the detection limit through dilution. Furthermore, it subjected the GC/ECD column to solids and other material that would not wash off the column or that physically damaged the column.

The use of Florisil (an activated magnesium silicate cleanup matrix) is well established for eliminating contaminants prior to analysis. Initial tests were performed with lab-fabricated columns prepared from standard Pasteur pipettes filled with a standard height of activated Florisil and anhydrous sodium sulfate. The Florisil itself was found to be appropriate, but the time spent preparing columns, the potential for uneven loading, the potential for deactivation of the Florisil during storage, and the lack of an adequate elution solvent reservoir space above the column were potential issues. Eventually, preloaded 6-mL Florisil extraction tubes were purchased from a commercial supplier, which also increased the available Florisil extraction media 30% to 1.0 g per tube. Following cleanup, the cleaned eluate was concentrated to a volume of exactly 1.0 mL and placed in sealed injection ampules for analysis.

Acid/permanganate extraction was examined to increase the maximum sample loading limit associated with the Florisil. In this method, the sample volume to be analyzed was washed with two volumes each of a 50% sulfuric acid and a 5% potassium permanganate solution. The extracts were then concentrated to exactly 1.0 mL, and placed in sealed injection ampules for GC analysis. While this proved to be an acceptable method for removing much of the contamination normally eliminated by the Florisil step, it did not show much improvement in eliminating the peak smearing caused by sample concentrations of more than 10% oil. In addition, the process generated a new waste stream, an aqueous-phase PCB waste, and also resulted in bulk solids and residuals coating the glassware used in the extraction, requiring careful cleaning procedures. Thus, the acid/permanganate method was used as a backup procedure, and was periodically used with samples with unusual material in their matrices.

3.2.1.2 Solid-phase Extraction

In some cases, it was necessary to extract bulk PCB solid wastes, such as wool felt, paint chips, and gelatinous samples, to determine initial PCB concentration and congener profiles. Soxhlet Extraction (EPA Method 3540A) is the baseline for PCB analysis on solids; however, this method is both time and waste intensive. An alternative is to use a sonication horn with successive solvent extractions (EPA Method 3550), which significantly cuts down the extraction time and reduces the amount of waste generated. Initial shakedown tests used three successive 10-mL washes with a 1:9 ratio of acetone and hexane on 1 g of sample material sonicated at about 80% of the maximum recommended power for the micro-horn for 10-min intervals. Analysis of the extraction solvent washes showed that less than 0.1% of the total PCB was present in the final wash; however, for all solid extractions, at least three washes were used.

This method was also used to analyze the carbon beds that filter PCBs in the offgas after the offgas passes through the condenser and impinger. As contamination of the beds was expected to be minimal, larger than 1-g quantities were used in the extraction to achieve lower detection levels.

Following the sonication extraction step, each solvent sample underwent Florisil cleanup to minimize degradation of the GC column by extracted non-PCB material, which provided better results. This step was necessary because the concentrated extraction solvent often contained hydrocarbon oils and other contaminants that were originally present in the sample.

3.2.2 Quantification Method - GC Analysis

PCB concentrations in sample extracts were quantified with a Hewlett Packard Model HP 5890 Series II GC with an ECD. The GC is equipped with automatic pressure control, on-column 1/4-in. injector, and is coupled with a 100-vial auto sampler. The GC/ECD was selected over a GC/MS (mass spectrometer) because it is very sensitive to the detection of chlorinated compounds. Some disadvantages of the GC/ECD are that it depends on elution time as its primary chemical identification mechanism and has no method of positively identifying a detected eluting compound as a PCB molecule or positively identifying a PCB molecule as a specific congener. The GC/MS has this ability, but since the critical parameter for the project was the detection and identification of completely treated samples, the low detection limit of the GC/ECD outweighed the congener identification abilities of the GC/MS.

The column used was a 30 m x 0.25 mm ID fused silica capillary column coated with DB-5 at 0.25 micron. Both ends of the column were broken off approximately once every three-run sets. The temperature/pressure program used for the majority of the project was based on similar programs used for analysis during the Guam operations. For each analysis, a 0.2 μL aliquot was shot (splitless) into the injector operating at 300°C. The aliquot was vaporized and flushed onto the column at 40°C. Initial hold time was 5 min, after which the column temperature ramped up 25°/min to 180°C, 5°/min to 300°C, and held for 10 min before cooling down. PCB elution occurred from about 180°C to 280°C. In some cases, when PCB levels were expected to be quite high, an extra 10 min of hold time at 300°C at the end of the run was added to allow time for any high concentrations of material to pass off of the column before the next sample was injected.

Quantification of the PCBs was performed according to a modified method used in Guam previously. The Dry Cleaning Manufacturer's Association (DCMA) PCB standard was used to calibrate the GC/ECD with a four-point calibration curve at orders of magnitude dilutions. The DCMA standard contains one representative congener from each of the homolog groups. These are IUPAC #'s 1, 11, 29, 47, 121, 136, 187, 194, 206, and 209. Average retention times were calculated for each of these congeners for a specific run, and midpoints were determined from this calculation to divide the chromatogram into 10 homolog retention ranges. On a typical chromatogram from an analytical set, every peak between congeners 1 and 209 was assumed to be a PCB peak unless otherwise verified, and each peak was assigned a homolog based on its retention time. Response factors were calculated for each of the 10 congeners, and these response factors were applied to the peaks in the appropriate homolog range. Calculated concentrations for each peak in a homolog range were added, and final numbers were reported in parts per million per homolog.

It is understood that for strict homolog identification, this method is expedient and not rigorously correct. According to *Analytical Chemistry Of PCBs* (Erickson 1992), there is significant overlap among the 10 homolog elution ranges in addition to varied ECD response among homologs. while this method will misidentify some congeners as nearby homologs and uses approximate response factors, it is still useful for interpretive purposes and is still generally accurate. In addition, examination of the typical congener elution profile indicates that this interpretation method errors on the conservative side, in that 1-CB, 2-CB, and 3-CB, the last homologs to be treated, all have higher potential to misidentify congeners of more highly chlorinated homologs, which have much higher ECD responses by weight of PCB. Thus, this method was determined to be acceptable for interpretive purposes and have a good value per cost over more rigorous methods.

3.2.3 Analytical Interferences and Corrective Actions

As discussed below, during the development and application of the analytical procedures, interferences were discovered, and steps taken to identify and eliminate or otherwise account for them.

3.2.3.1 Oil Matrix Interferences

Initially, quick analytical tests were designed for high- to medium-PCB-concentration samples that required as little preparation as possible. Oil-phase samples were to be diluted with hexane and shot directly into the GC/ECD without any further preparation. This method was tested and found to be unsatisfactory for this matrix. Chromatograms generated from this method showed a rapidly climbing baseline after the 2-CB or 3-CB homolog range and some overloading, indicating contaminants and possibly water present. In addition, some column defunctionalization was noted at a more rapid pace than expected, and the column was eventually replaced. To protect the analytical equipment and provide more consistent results, it was decided that sample preparation in the form of Florisil or other cleanup would be performed on all samples prior to injection on the GC/ECD. The Florisil cleanup method also seemed to function well for drying any samples that had contacted or were lightly contaminated with water. This is particularly important for the organic phase from a liquid extraction of an aqueous PCB sample.

3.2.3.2 Equipment Interferences

Part way through laboratory-scale testing in the 2-L reactor, a contaminant appeared in analytical testing on the GC/ECD chromatograms. The contamination was characterized by a set of 5 major peaks, and 10 to 20 minor peaks, in the range of the 7-CB to 10-CB homologs and sometimes as high as 2 ppm per homolog of these four. Various analyses indicated that the detected peaks were always of similar ratio to each other, but were not present in an absolute ratio to the amount of sample that was Florisil cleaned. The contaminant was present in oil and in all Florisil-processed solvent blanks, and was thus determined to have come from some handling error during cleanup or preparation. It was determined that the contaminant was in the vials used to collect and concentrate the eluant from the Florisil cleanup. The contaminant was found to be some form of plastic or plasticizer in the thread-reinforced tissues used in the final drying step of the glassware cleaning procedure for the vials immediately following an acetone rinse. The plasticizer was extracted from the tissue and plated out on the glass as residual liquid in the vials evaporated. The material slowly built up on the vials and was eventually concentrated enough to leach into the cleaned sample placed into the vial, and appear on the GC/ECD chromatogram. Liquid/solid extraction of a piece of laboratory tissue generated the same series of peaks on the GC/ECD. The procedure was modified to air dry the vials following washing, which eliminated the contaminant.

3.2.3.3 1-CB 4 Peak Interference

Contamination in the lower chlorinated homolog range has always been critical due to the low detection limit of these species and the fact that the last homolog to be destroyed is usually 1-CB. Analysis of LW-110 and LW-104 untreated media blanks showed a noise in the 1-CB range consisting of 4 very small peaks. While these peaks are on the lower limit of detection through the GC/ECD, the response factor of 1-CB is low enough that after analytical calculations for standard preparation dilutions, the total noise concentrations can be as high as 10 to 20 ppm of 1-CB. The noise is similarly present in samples of the treated oil slurry, although it does not appear in the hexane solvent blanks cleaned with Florisil and prepared as if they were oil samples. Thus, the noise must reside in the oil phase itself, and not be due to BCD processing, sample cleaning, or preparation. Despite continued effort, no method was found to filter out this noise or find alternatives for analysis.

The total concentration of the noise (interpreting it as if it were actually 1-CB homolog) is quite constant; thus, it can be corrected for by using blank subtraction in the cases where a blank was specifically tested alongside the sample. In most cases, the oil blank showed apparent 1-CB concentrations from 6 to 12 ppm. In reporting the data, only the uncorrected values are given. However, in interpreting the data to determine whether or not the run was successful (i.e., treated product contains less than 2 ppm PCB per resolvable congener), the "corrected" concentration was used. Furthermore, before such runs were declared successful, the GC chromatograms were closely examined to verify that the profile and relative ratios of the contaminant peaks were consistent with those seen in the clean oil blanks.

4.0 Bench-scale Treatability Testing

Although existing information on the BCD process provided approximate operating conditions for the vessel materials application, bench-scale treatability tests were conducted to determine those conditions more exactly for these specific wastes and to more thoroughly investigate the process chemistry. Parameters investigated included BCD reagent dosages, temperature, reaction time, reaction media, and alternative chemical additions. With the 2-L STR system, testing could be conducted on a highly controllable scale for quickly determining the efficacy of proposed concepts. Additionally, with the 2-L system, material balances could be accurately determined. The results of the treatability testing were fed into the pilot-scale system design, which is described in Section 5.0.

This section describes the 2-L bench-scale STR system, the testing strategies, and the results of the testing. The bench-scale test results have been organized into six groupings, based on the objectives of the tests and the waste form treated. With the exception of the Paint Chip Runs, the 2-L bench-scale tests were conducted with wool felt as the source of PCB. The six grouping are listed below:

Shakedown Runs	SD1, SD2, SD3, SD4	Pre-recordable tests to line-out testing, sampling, and analytical procedures
Baseline Runs	R1, R3, R4, R5, R6	Tests to examine the baseline BCD process
Proprietary Reagent Runs	R2, R7, R8, R9	Tests to examine modifications to baseline BCD process
High Waste Loading Runs	R10, R12, R14, R16, R18	Tests to examine maximum waste loading
Paint Chip Runs	R15, R17, R19, R20	Tests using PCB-containing paint chips as the waste form
Miscellaneous Runs	R11, R13, R21	Tests to examine BCD processing alternatives

Within the discussion under each grouping of runs, information is provided that summarizes the operations of each run and describes the process chemistry and analytical results.

4.1 2-L Stirred-Tank Reactor (STR) System

The STR consists of a 2-L stainless steel reactor, a three-port stainless steel reactor head, a mixing assembly, head and body heating mantles, and a rheostat for temperature control. The center port houses the agitator shaft. One offset port is fitted with a multi-functional U-tube that includes provisions for sampling, purging, and pressure relief. Nitrogen gas (or another inert gas) is injected as purge gas. The leg of the U-tube is submerged in 5 to 10 cm of oil to ensure that the reactor system is not overpressurized and to act as a scrubber medium for offgas or liquid vented from the reactor if an overpressure event did occur. The final port is used for temperature monitoring and serves as the offgas vent and scrubber system. One thermocouple is placed into the reaction medium, and one is used to monitor offgas temperature.

The offgas vent system includes a moisture test receiver (MTR), a water-cooled condenser, an impinger, and a carbon trap. The MTR collects the condensate from the condenser. From the MTR, the condensate can either be removed from the system or returned to the reactor through a return line to the offgas port. Offgas temperature is monitored at the top of the MTR, upstream of the condenser. The condenser is cooled with either tap water or chilled water. The 2-L STR system is designed to operate at temperatures up to 400°C and pressures up to up to 6 mm Hg. All but one of the screening tests have been conducted in this system. The 2-L STR system is shown in Figure 4.1.

4.2 Operating Strategies (Test Approach)

The feed constituents available for testing range from soft solids to hard brittle solids in a wide variety of sizes. Because the waste forms tested degrade and disintegrate upon heating in the oil matrix, size reduction was limited to the extent necessary to facilitate the physical operations (i.e., reactor loading and agitation). The operational setup is similar to the liquid-phase reactors being used at BCL and by other groups with BCD testing experience. A series of tests with the 2-L STR were also conducted by PNNL with PCB in Guam (May 1995). The operating strategy outlined below has been successfully demonstrated.

Detailed operating procedures for the 2-L STR, summarized here, are documented in the Safe Operating Procedure. For each run conducted in the 2-L STR, the feed consists of a bulk reaction medium, BCD reagents, and the target contaminated constituent(s). The bulk medium, consisting of either LW-104, LW-110, Fuel Oil #6, or a similar medium, is placed into the reactor. The reagents and PCB-contaminated constituents are then added. The final volume of material inside the reactor occupies about 50% to 70% of the total reactor volume. After loading, the reactor is sealed and the offgas system is assembled. Before the run is initiated, the reactor and offgas system are pressure checked to ensure that the system is leak free. The flow of purge gas is initiated and maintained throughout the run at a flow rate as low as possible. Next, the heat cycle is initiated. When the contents of the reactor degrade sufficiently, the agitator is engaged and the reactor is heated and held at target operating temperatures.

Samples are pulled during the run as specified in the run plan. The sampling apparatus, which consists of a sampling probe (1/4-in. tubing) attached to a syringe, is thoroughly cleaned prior to sampling. For sampling, the agitator motor is shut off to avoid striking the sample probe. The valve on the sample port is quickly opened, and the sample probe inserted. A syringe attached to the probe is used to quickly withdraw a sample (approximately 5 mL). The sample probe tip is placed in a sample bottle, and the sample is ejected.

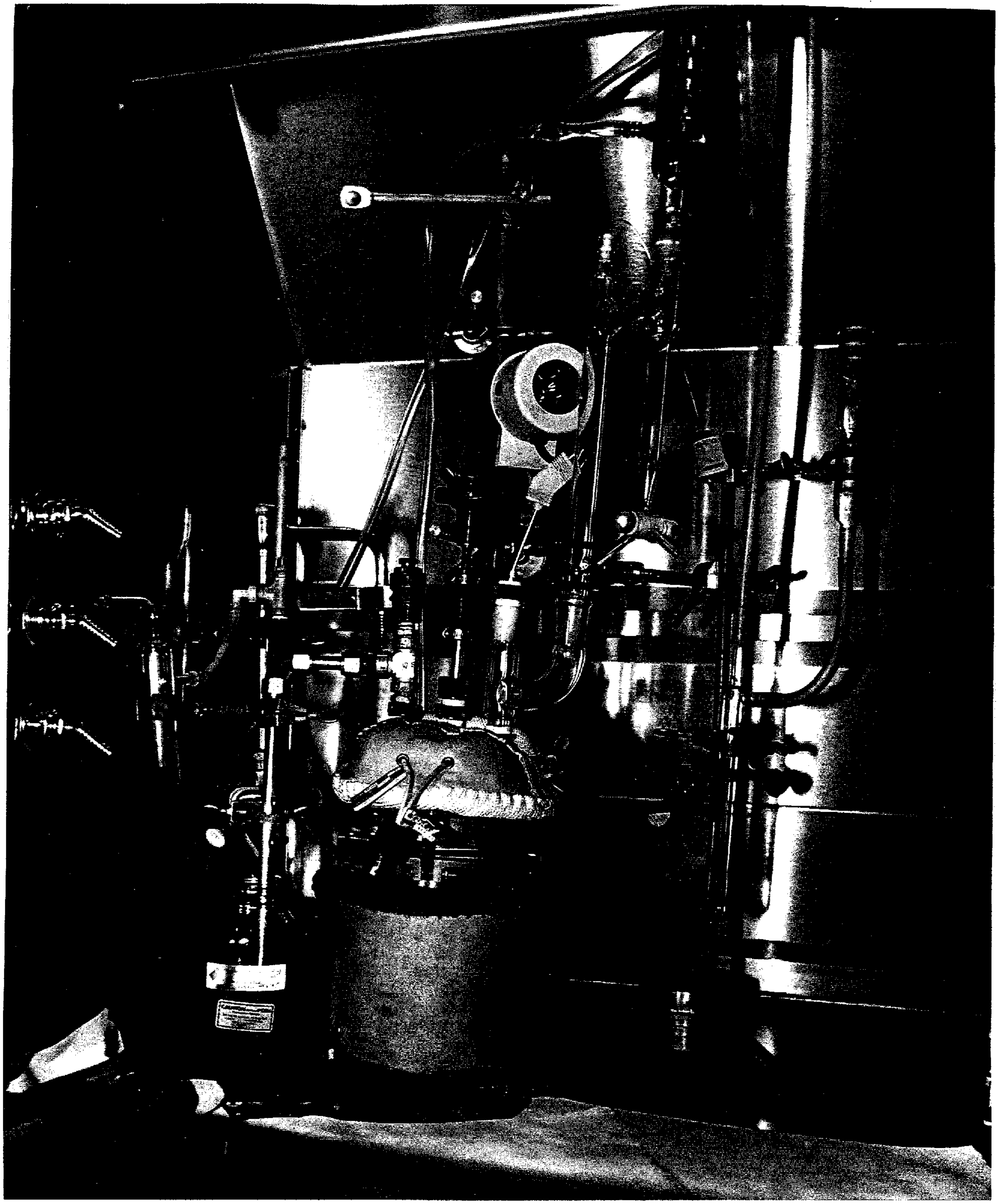


Figure 4.1. 2-L Stirred-Tank Reactor

Cooldown is accomplished by turning off the heat and removing the reactor head heating mantle. Upon completion of the run and after cooldown, for material balance purposes, the inside of the offgas system is rinsed with a solvent to collect any PCBs that may have condensed there.

Material balances were performed by comparing the mass of the reactor contents at the start of the run with the sum of the masses of the process products and residuals. These products and residuals included the treated contents remaining in the reactor, organic and aqueous-phase condensates, samples, residuals adhering to the sampling probes, and the mass increase of the GAC bed. Material adhering to the reactor head, MTR, condenser, and offgas tubing was not accounted for.

4.3 Shakedown Runs

Four shakedown tests were conducted with PCB-containing wool felt in the 2-L STR before record runs were initiated. Data collected from these tests are not reportable since the QAPP was not approved when the runs were conducted. The main objectives of these runs were to shake down the test equipment, refine sampling techniques, and generate product sample for refinement of extraction and analytical techniques. Activities were focused on developing extraction and analysis procedures for the product samples because the PCB concentration in the treated material was considered to be the critical analytical parameter.

Samples were successfully collected during the run at temperatures of 300°C and 350°C. Preliminary analytical results indicated that significant PCB destruction occurred at 300°C. After the reactor operated at 300°C for 2 hr and 350°C for 2 additional hours, no PCB was detected in the treated product. The results from the shakedown testing also showed that very little condensate was generated from treatment of wool felt feed. In comparison, during testing in Guam with the 2-L STR, as much as 500 mL of condensate were generated from treatment of 1400 mL of feed.

Another key finding from the shakedown tests showed that the average PCB concentration in the wool felt was approximately 14% by weight, compared with the historical average of 35% by weight based on analytical data from PSNSY. Results from shakedown testing also indicated that significantly greater concentrations of base (NaOH) were required to effect complete dechlorination of PCBs than the baseline weight ratio (NaOH:PCB) of 2.5:1. It was surmised that the wool felt matrix consumed NaOH as it was digested and hydrolyzed at reaction temperatures. Additional NaOH may also be consumed in reactions with the hydrocarbon oil reaction medium.

One shakedown test was also conducted using a Battelle proprietary reagent that is being tested as a reagent for allowing lower operating temperature in the STR (see Section 4.5). This test showed that near-complete dechlorination of PCBs may have been accomplished at temperatures below 300°C.

4.4 Baseline BCD Testing

The objectives for initial BCD testing included developing and demonstrating a reproducible, successful baseline recipe for treating the wool felt matrix. This baseline recipe would serve to compare the effects of major matrix changes in the BCD reagents, feedstock, or medium and also provide an acceptable starting point from which optimization might be performed.

Baseline BCD runs were conducted with wool felt at the temperatures and reagent loadings determined to be effective on other waste matrices in previous BCD Stage 2 work (Schmidt et al. 1996) and on wool felt during the shakedown testing. The following starting baseline conditions were used: LW-110 oil as the reaction medium; a mass ratio for NaOH to PCB of 6.25:1 (raised from 2.5:1 per preliminary results from shakedown testing); a mass ratio of hydrogen donor oil, LW-104, to PCB of 4.25:1; and a catalyst concentration in the final matrix of approximately 0.75% by weight. For these tests, wool felt made up approximately 13% of the mass of the reactor contents, and the ratio of reaction oil to wool felt was about 6:1. After a baseline run was conducted, the effects of catalyst and hydrogen donor oil were tested by omitting them from the feed matrix. Additionally, the use of another hydrocarbon oil, Fuel Oil #6, was tested. A duplicate run of the baseline case was conducted to examine the repeatability of both the analytical results and the operability of the system.

Results from the baseline testing (Table 4.1) show that for the wool felt matrix, neither hydrogen donor oil (LW-104) nor catalyst are necessary and do not have a perceptible effect on the rate or extent of PCB destruction for treatment of wool felt. It was also shown that operation and analytical results were repeatable from run to run.

4.4.1 Run Summaries

4.4.1.1 Run R1 (10/18/95) - Baseline Run

The objective of R1 was to conduct a test with the wool felt matrix at BCD baseline reagent loadings (including catalyst), temperatures, and hold times. Run conditions were 2 hr of operation at 250°C, 300°C, 350°C. The total time for completion of this run was approximately 8 hr. During the initial part of R1, the system vibrated significantly as a result of wool felt pieces (approximately 2 x 2 x 1 cm) knocking against the agitator. As the temperature of the reactor increased to about 120°C - 150°C, the shaking stopped, apparently as a result of wool felt pieces dissolving and disintegrating. Aqueous-phase condensate (water) did not come off until the reactor temperature was approximately 200°C. During the course of the run, 17.9 g of aqueous condensate and 8.7 mL of organic condensate were generated and collected. The organic condensate contained 2500 ppm PCB. Upon completion of the run, the reactor contents formed a slurry that can be described as a homogeneous gel.

4.4.1.2 Run R3 (10/27/95) - No Hydrogen Donor

Run R3 was similar to the baseline run (R1) but without the addition of the hydrogen donor. This testing was conducted in a effort to minimize complexity in the matrix required for effective PCB destruction, in this case, LW-104, a medium-boiling-point hydrocarbon. In R3, there was less organic and aqueous condensate during the later target reaction temperatures than in R1, and this is partially attributed to the stricter control over the MTR temperatures during the run. In this test, the stirrer was

Table 4.1. Summary of Baseline BCD Tests in 2-L Reactor

Run No.	Run Conditions (Temp., Time)	Successfully Treated (yes/no/AE[a]), Uncorrected[b] PCB Concentration, ppm	Wool Felt (g)	Est. PCB (g)	Reagent Loadings					
					LW-110 (g)	LW-104 (g)	Other (g)	NaOH (g)	Catalyst (g)	Battelle Proprietary Reagent (y/n)
R1	 250°C, 2 hr 300°C, 2 hr 350°C, 2 hr	Feed 16,000 No, 7100 No, 1200 Yes, 16	143	20	791	85.7	None	125	7.5	No
R3	 250°C, 2 hr 300°C, 2 hr 350°C, 2 hr	Feed 17,000 No, 10,000 No, 1600 Yes, 12	143	20	796	None	None	125	7.5	No
R4	 250°C, 2 hr 300°C, 2 hr 350°C, 2 hr	Feed 15,000 No, AE No, 280 No, <20	143	20	None	86	889, Fuel Oil #6	125	7.5	No
R5	 250°C, 2 hr 300°C, 2 hr 350°C, 2 hr	Feed 17,000 No, 6700 No, 810 Yes, 15	144	20	786	85.3	None	125	None	No
R6	 250°C, 2 hr 300°C, 2 hr 350°C, 2 hr	Feed 16,000 No, 9500 No, 1500 Yes, <2	144	20	788	83.1	None	125	7.5	No

(a) AE analytical error, data not reportable.
(b) Interference and contamination have not been subtracted out.

purposely left on overnight to determine the state of the product if stirred continuously during cooldown. A highly stable gel was formed without any observable separation of solids and oil. It was concluded that prolonged stirring of the reactor during cooldown should be avoided in future operations.

4.4.1.3 Run R4 (11/8/95) - Fuel Oil #6 as Reaction Medium

R4 was similar to the baseline run (R1), with catalyst and hydrogen donor, but used Fuel Oil #6 instead of LW-110 as the reaction medium. This run was conducted based on reported success in Japan with Fuel Oil #5. Fuel Oil #6 is less expensive than LW-110 and contains a natural source of the BCD catalyst and hydrogen donor material, potentially eliminating the need for some reagent addition when required by the matrix. During the heatup portion of this run, vigorous boiling occurred between 200°C and 220°C, and the reactor boiled over. While the reactor was operating at 350°C, vigorous refluxing was observed—on the order of ~60 mL/min—which required greater heat input to maintain temperature relative to runs with LW-110. When the reactor was disassembled after completion of the run, the reactor contents had a very high viscosity, meaning very little, if any, of the material would be available for recycle for additional runs. Analytical results showed that after 2 hr of treatment at 300°C, greater than 98% PCB reduction was obtained, with the treated product containing approximately 300 ppm PCB (primarily mono- and dichlorinated). After 2 hr at 350°C, approximately 10 ppm total PCB remained in the sample. Analytical testing was difficult due to the thick consistency of the samples. All of the samples had to be extracted and treated as solid samples. Even though this run generated relatively large quantities of offgas, analysis of the carbon bed, which serves to polish the offgas, showed that the GAC contained less than 0.1 ppm total PCB.

4.4.1.4 Run R5 (11/14/95) - No Catalyst

Limited testing with the bench- and full-scale STR in Guam indicated that catalyst was necessary in the BCD process for complete destruction of PCBs with the wastes treated in Guam. R5 was conducted to determine the effect of omitting catalyst from the wool felt matrix. A rigorous material balance was also performed. The run was conducted similarly to the other baseline runs. During the run, 18.2 g of aqueous condensate and 7 mL organic condensate were generated. Analysis of the carbon bed showed that the GAC contained less than 2 ppm total PCB. Comparison of condensate generation rates and operations between Runs R1 and R5 showed that operating differences are minimal. From the material balance calculations, 98.4% of the material added to the reactor was accounted for.

4.4.1.5 Run R6 (11/15/95) - Baseline Run Duplicate

The purpose of R6 was to duplicate all conditions in R1 as closely as possible to examine the repeatability of the process and experimental procedures, including analytical procedures, and to complete a rigorous material balance. R6 was conducted nearly a month after R1 to determine if testing and analytical methods changed with time.

For this run, a total of 19 g of aqueous condensate and 6.3 mL of organic condensate were generated and collected in the condenser. The organic condensate contained 1300 ppm PCB. At the start of the run, 1148 g of material were placed into the reactor. Of this total, 98.8% of the contents were accounted for at the conclusion of the run by material balance calculations.

Comparison of condensate generation rates and operations between Runs R1 and R6 showed that operating differences are minimal and that operations are similar. For R6, approximately 25% less organic condensate was collected, likely a result of the more quiescent water removal between 190°C and 250°C. Figure 4.2 shows the condensate and temperature profiles as a function of time for Runs R1 and R6.

4.4.2 Process Chemistry

The total PCB detected in the analytical results was summed for each sample for R1 and R6, and the results are shown in Figure 4.3 as $\mu g/g$ of PCB per gram of sample at each of the sampling intervals. It must be noted that the sampling intervals cannot be summed to yield elapsed time, as there are transitional times not accounted for while the process is heating from one hold temperature to the next, which usually takes from 20 to 40 min.

The PCB concentration profiles of the two tests both appear to be of the same character and magnitude. It is apparent that the baseline method is repeatable, in that the rate of destruction follows nearly the same profile. Minor discrepancies, specifically at the samples in the 250°C hold temperature, may be due to discrepancies in the heatup cycle from room temperature to 250°C or possibly from variations in the wool felt feedstock. Regardless, the time at temperature to extinction of the PCB appears to be very similar; it requires at least 1 to 2 hr at 350°C to achieve total destruction at this loading with the baseline BCD recipe. Thus, the criterion for reproducible, successful testing was achieved, and this particular loading was selected as the baseline BCD for testing modifications and optimization comparisons. This also provided an indication of the potential variability and uncertainty with which to evaluate improvements, as modifications that provide minor improvements may be indistinguishable from standard process variability.

While complete destruction of all of the PCB congeners (i.e., need to achieve < 2 ppm/congener) was the major focus of the screening studies, a second focus was to obtain a greater understanding of the mechanisms of the dechlorination reactions by examining the homolog shift of the PCBs during the destruction process. Analytical results for all of the runs indicated that PCBs in the process matrix were reduced from higher chlorinated homologs to lower chlorinated homologs and then, in the case of a successful run, to extinction. In Figure 4.4, the 10 PCB homolog concentrations are shown at each of the sampling intervals for Run R1.

The homolog profile from Run R1 shows a distinct shift towards lower homologs in addition to actual destruction, which supports the assumption that BCD consists of a set of singular dechlorination reactions. It is interesting to note that the homolog profile for the "time zero" sample, which was taken when the reactor reached 250°C, resembles a slightly modified Aroclor 1260 mix with 6- and 7-CB

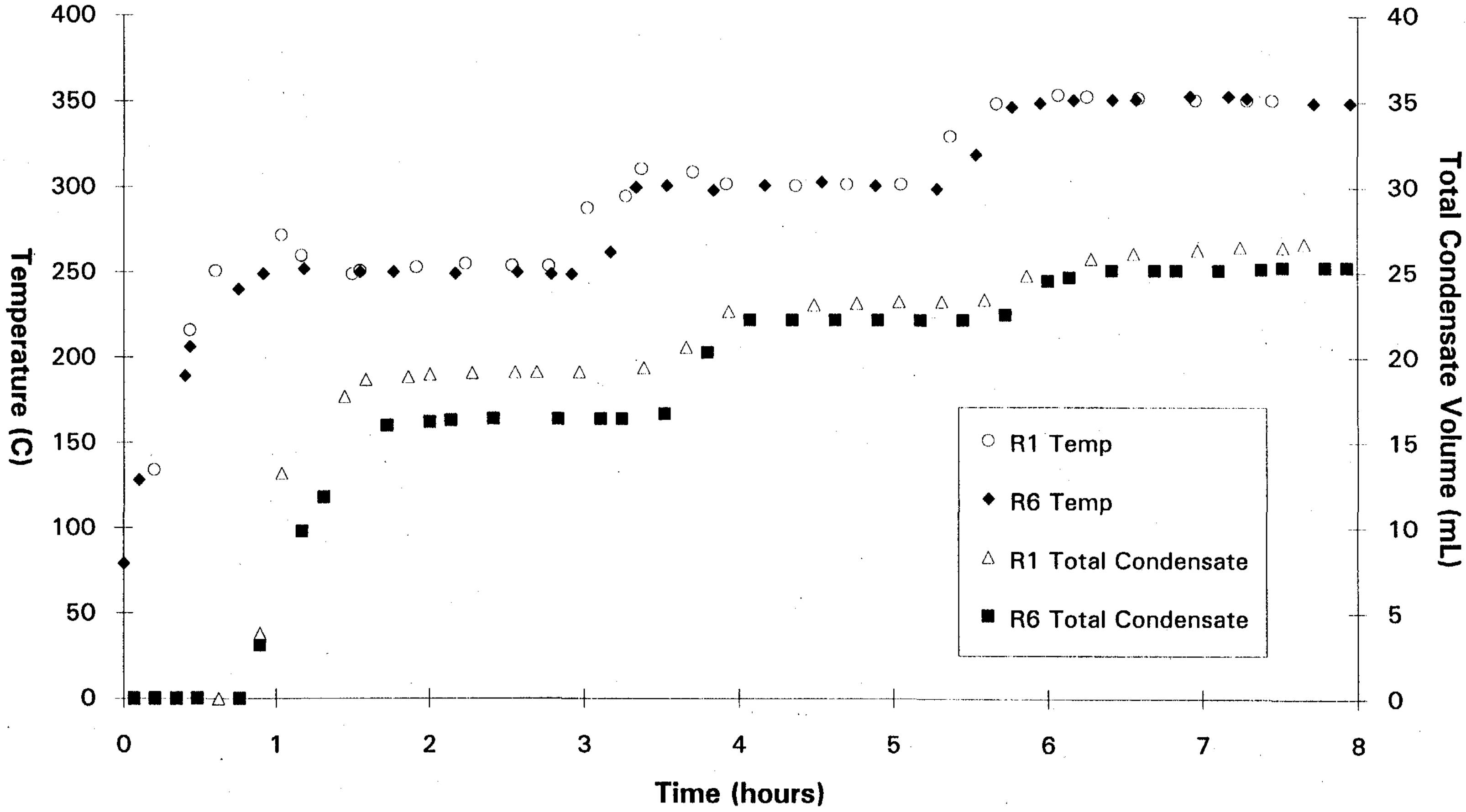


Figure 4.2. Temperature and Condensate Profiles for R1 and R6

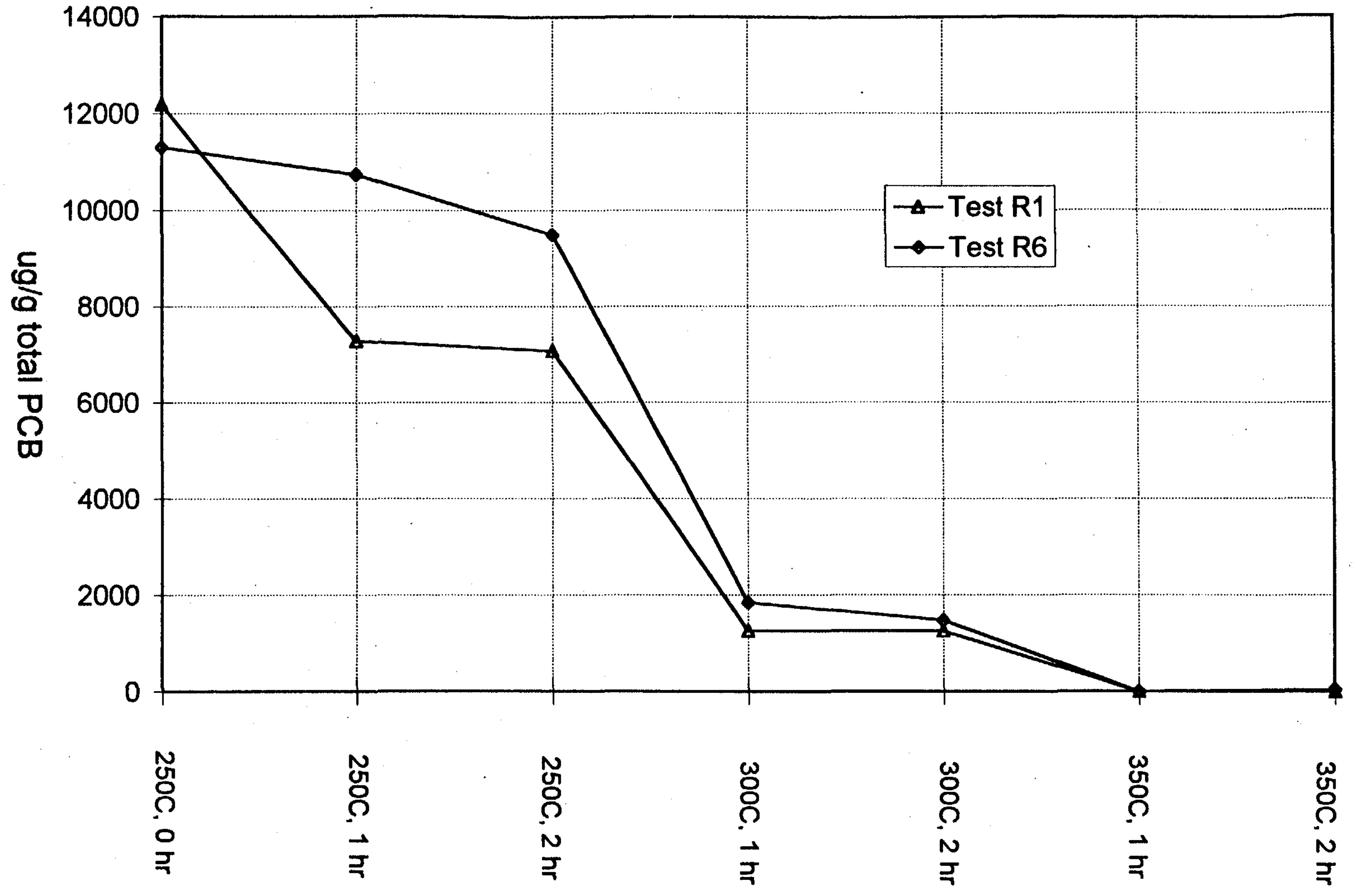


Figure 4.3. Total PCB Concentration as a Function of Time for Runs R1 and R6

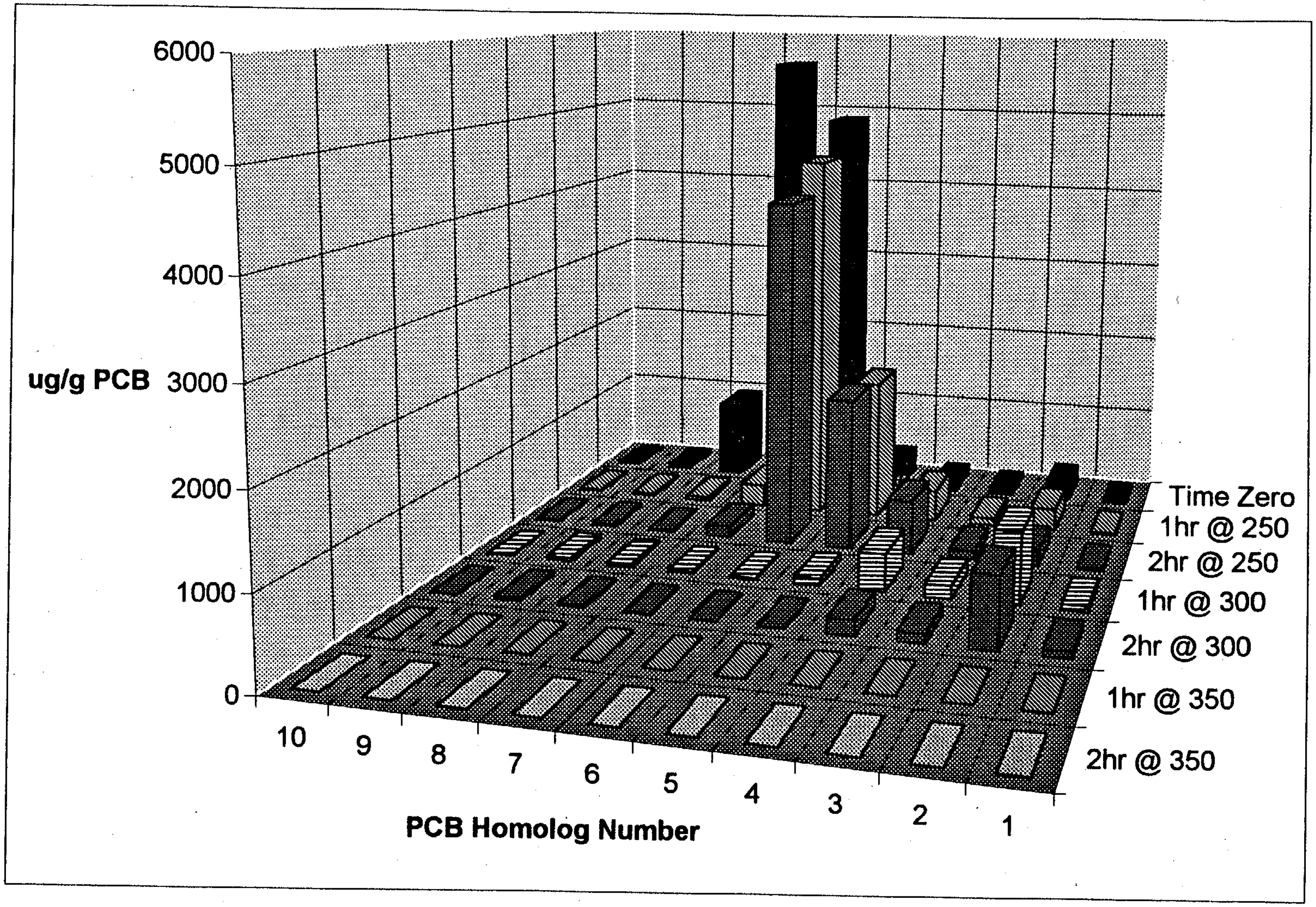


Figure 4.4. PCB Homolog Profile as a Function of Time and Temperature for Run R1

homologs making up about 80% of the population rather than the Aroclor 1268 mix that was suspected to be in the feed, consisting primarily of 8- and 9-CB homologs. A homolog profile of the wool felt feedstock yielded a profile of 8.4% 10-CB, 31.8% 9-CB, 48.1% 8-CB, 9.5% 7-CB, and trace amounts of 1- through 6-CB, which appears very similar to a slightly degraded Aroclor 1268 profile. This was unusual, as no significant PCB destruction was expected below 200°C.

In testing conducted after Run R1, samples were often taken at temperatures near 120°C, (when the wool felt in the oil disintegrated to the extent to allow for the collection of a representative sample). Figure 4.5, which shows the homolog profile from Run R5, includes the profile from a sample taken at 120°C, which displays the same characteristic Aroclor 1268 profile shown in standard feedstock analysis. As in R1, the 250°C sample in R5 shows significant shift to a profile much more characteristic of Aroclor 1260. Repeated confirmation of this phenomenon from other tests, both with and without modification to the baseline BCD reagents, indicates that the initial dechlorination of 8- to 10-CB occurs very rapidly, and is most likely of a different mechanism than dechlorination of 7-CB homologs and below.

4.4.2.1 Hydrogen Donor

Run R3 was conducted similarly to the baseline test, R1 (and R6), except LW-104 was not added to the matrix. Total PCB concentration versus time for the baseline runs (Runs R1 and R6) and R3 is shown in Figure 4.6. In comparing the runs, there appears to be few differences. The initial PCB concentration for R3 at time zero at 250°C appears to be slightly higher than both R1 and R6; however, this may be explained by a difference in the wool felt used for the runs, or slight differences in the heating profiles for the tests. Regardless, the time to extinction of the PCB for all three runs appears to be the same for total destruction of the PCB.

Past BCD testing with other matrices has shown the dependence of the process on a successful hydrogen donor reagent. However, it is surmised in this case that the decomposing wool felt may potentially act as the hydrogen donor. Previously, many other organics have been tested as potential hydrogen donor reagents with varied success. Thus, the success of the wool felt is not surprising. It is doubtful that the wool would be useful as a BCD reagent elsewhere; however, wool felt may possibly be combined with other waste forms generated from Navy vessel decommissioning, such as PCB-contaminated paint chips and other materials, thereby reducing the need for extra reagents that would be required to process the waste forms separately.

4.4.2.2 Catalyst

Figure 4.7 shows little or no difference among the baseline runs with catalyst (R1 and R6) and the and no-catalyst Run (R5). These observations support that this particular catalyst, which was used in previous BCD testing, is either unnecessary or redundant in this matrix. This would point towards the uncertainty surrounding the wool felt and the effect of its organic decomposition on the chemistry of the BCD process. In some of the testing after R5, the catalyst was eliminated to meet the objective of minimizing the complexity of BCD recipe.

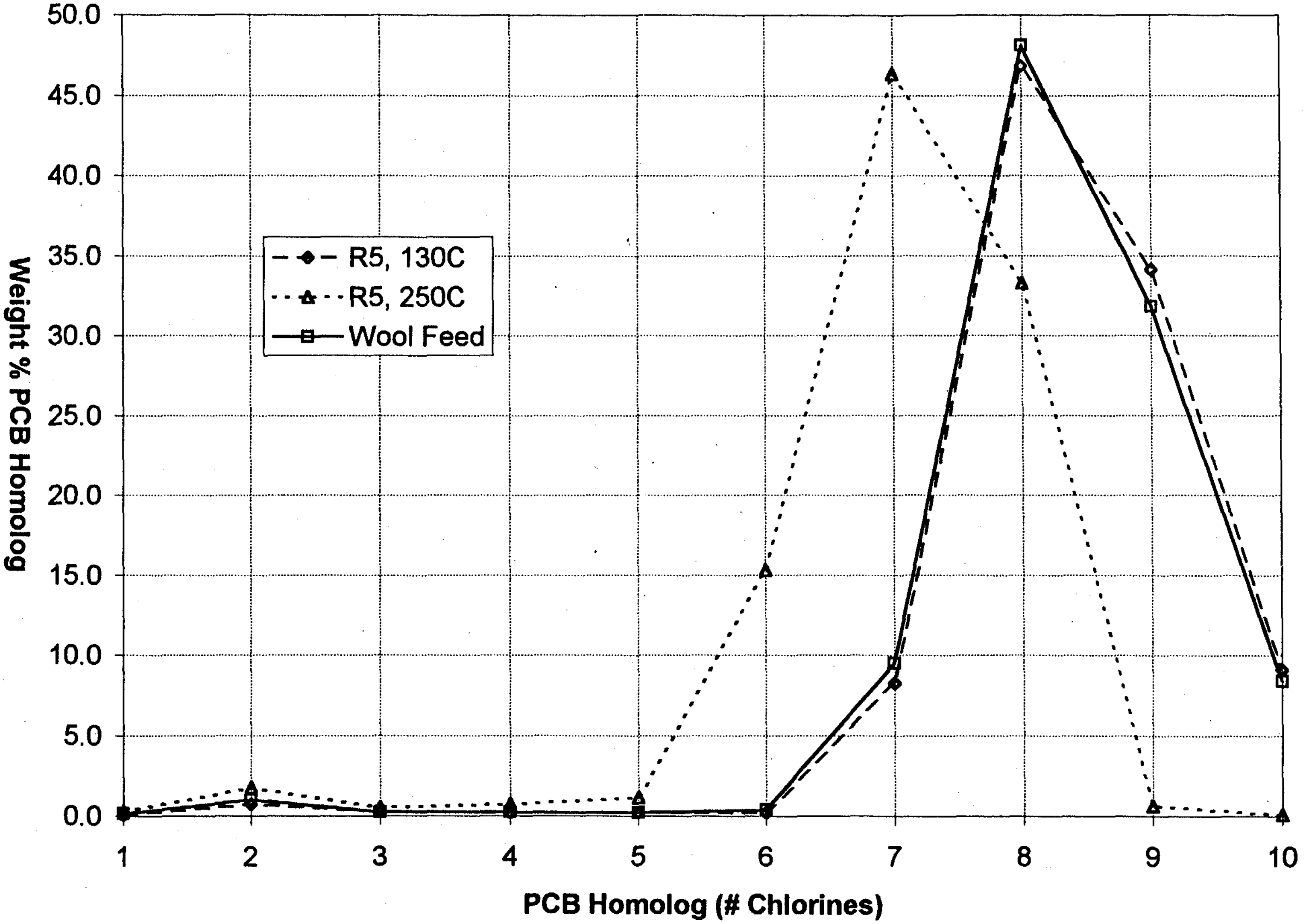


Figure 4.5. PCB Homolog Profile as a Function of Time and Temperature for R5 as Compared to Wool Felt

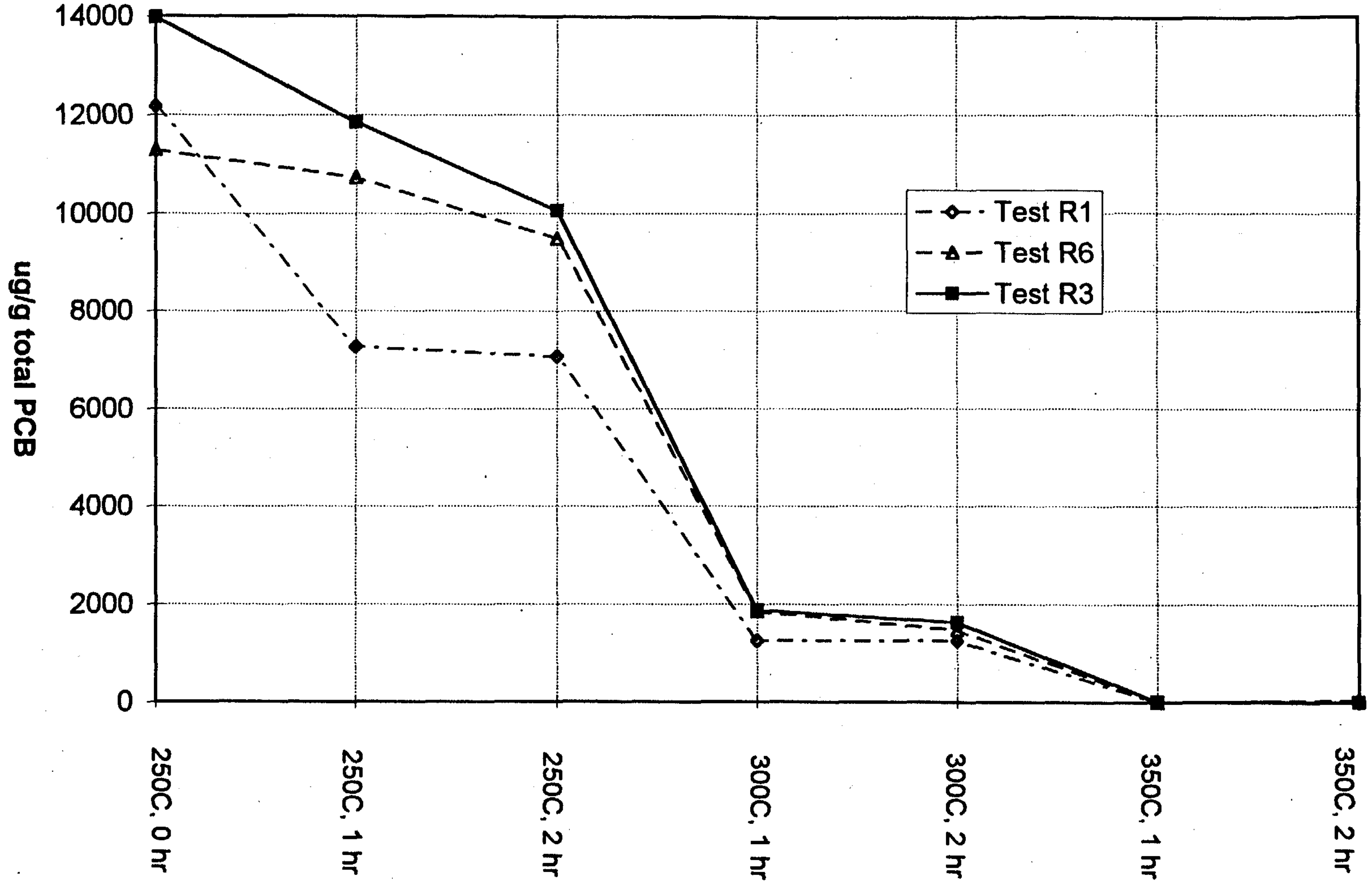


Figure 4.6. Effect of Removing Hydrogen Donor Oil (LW-104) on PCB Destruction (R1 and R6 vs. R3)

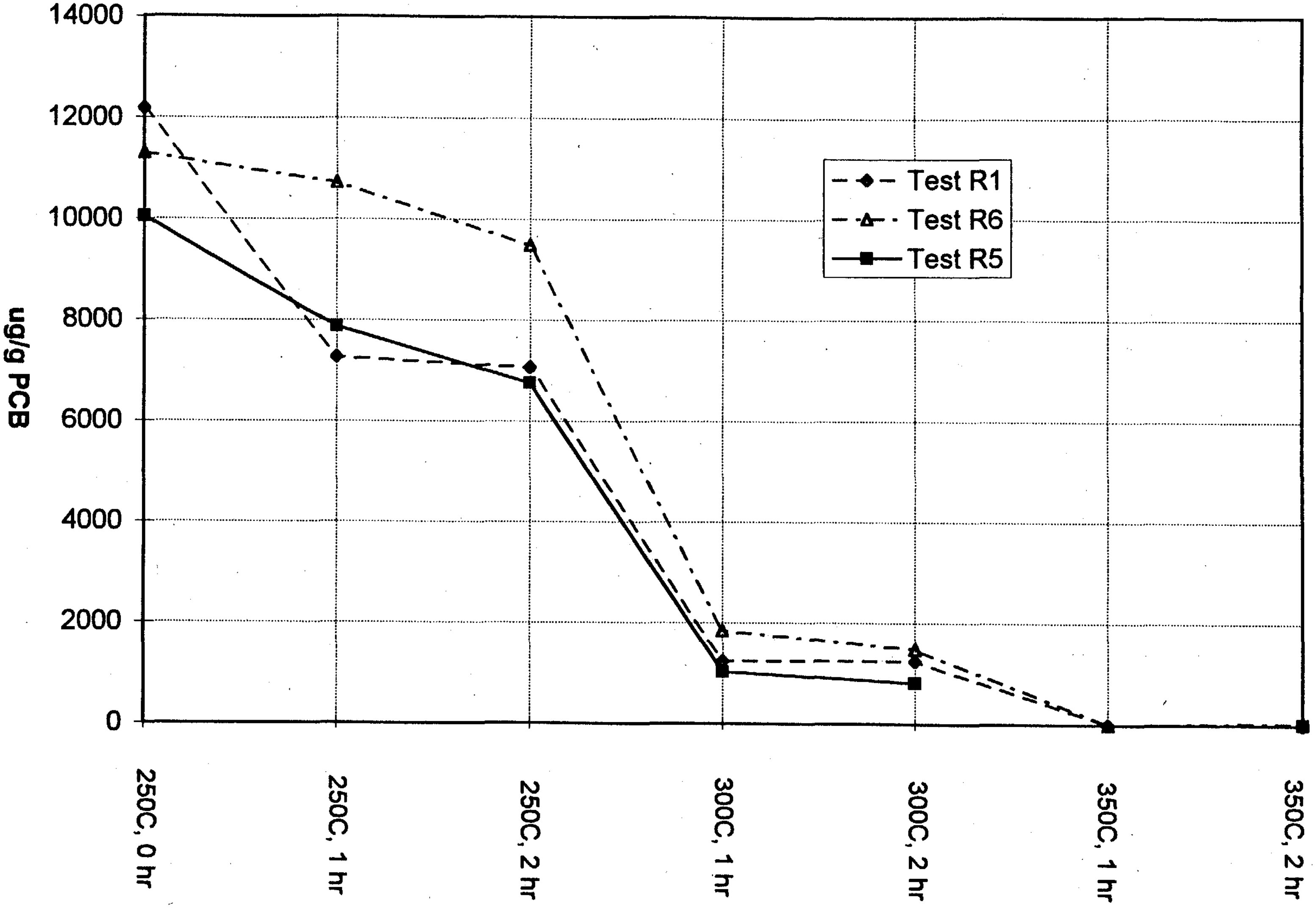


Figure 4.7. Effect of Removing Catalyst on PCB Destruction (R1 and R6 vs. R5)

4.5 Battelle Proprietary Reagent Runs

Considering the potential benefits of STR operation at lower operating temperatures (i.e., lower costs, increased safety, and reduced volatilization of PCB), an idea was developed for reducing the BCD reaction temperature, and an invention report was filed on a proprietary reagent developed by Battelle staff (at BCL and PNNL). Testing with the new reagent indicated that significant PCB destruction occurs at much lower temperatures than the baseline BCD process, reducing nominal operating temperatures to as low as 250°C or 275°C. The use of the Battelle reagent allowed LW-104 to be substituted for LW-110 as the primary reaction medium, which yielded better separation between the solids and the oil phase at the conclusion of a test and ensured that the reaction medium could also act as the hydrogen donor, if needed.

With the reduced operating temperature, the system can be operated below the auto-ignition point of the oil medium, rather than above it as with current BCD technology. Lower temperatures also reduce the propensity for distillation of PCB, and results in more quiescent return of overheads to the reactor, particularly if some of the organic condensate consists of semi-volatile components. Process cycle time can also be effectively reduced, along with the total required energy input into the reactor by effecting dechlorination at lower reaction temperatures. Furthermore, operation at lower temperatures can reduce the quantity of water removed from the reactor. For R2, over 50% of the aqueous condensate collected from the run was collected between 270°C and 350°C. Water removal during reactor heatup can create operation difficulties and limit the heatup rate. Therefore, allowing the reactor matrix to hold on to the water while operating at lower temperatures can cut down process upsets and processing time in addition to reducing the volume of aqueous condensate requiring polishing prior to release.

Test conditions from the initial Battelle reagent testing are shown for the wool felt matrix in Table 4.2. With the Battelle reagent, complete dechlorination is achievable at temperatures below 300°C.

4.5.1 Run Summaries

4.5.1.1 Run R2 (10/25/95) - Baseline Battelle Reagent Run

The objective of R2 was to test modifications to the BCD recipe and compare the results with the baseline run (R1). Both catalyst and hydrogen donor oil (LW-104) were added to the matrix in this run to ensure comparability with R1. Run conditions were 2 hr of operation at 250°C, 300°C, 350°C. During the run, 31 g of aqueous condensate and 9.3 mL of organic condensate were generated. This aqueous-phase condensate generation is nearly twice that of R1. The increase is most likely due to the presence of water in the Battelle reagent. After completion of the run, the agitator was turned off when the temperature of the contents was between 250°C and 300°C. The following day, the reactor was opened, and two distinct phases were present: a separated oil phase with a slight blue color and a hard,

Table 4.2. Summary of Battelle Propriety Reagent Runs

Run No.	Run Conditions (Temp., Time)	Successfully Treated (yes/no), Uncorrected[(a)] PCB Concentration, ppm	Wool Felt (g)	Est PCB (g)	Reagent Loadings					
					LW-110 (g)	LW-104 (g)	Other (g)	NaOH (g)	Catalyst (g)	Battelle Proprietary Reagent (y/n)
R2		Feed 16,000	143	20	796	84.5	None	62.7	7.5	Yes
	250°C, 2 hr	No, 3300								
	300°C, 2 hr	Yes, 7.5								
	350°C, 2 hr	Yes, <7								
R7		Feed 16,000	144	20	None	851	None	63.3	7.5	Yes
	190°C, 4 hr	No, 7300								
	250°C, 4 hr	No, 1400								
R8		Feed 14,000	144	20	None	851	None	63.3	7.5	Yes
	275°C, 1 hr	No, 64								
	280/287°C, 1 hr	Yes, 12								
R9		Feed 18,000	143	20	781	None	None	31.9	7.6	Yes
	250°C, 2 hr	No, 5100								
	300°C, 2 hr	No, 4400								
	350°C, 2 hr	No, 2700								

(a) Interference and contamination have not been subtracted out.

semi-crystalline solid phase. Agitation suspended very fine particles and rendered the liquid phase opaque even after centrifugation. Material balance calculations showed that 98.1% of the initial mass was accounted for. Total losses amounted to about 22 g. It is suspected that holdup in the offgas components (i.e., MTR, condenser, and tubing) and noncondensible vapor generation comprised the bulk of the material unaccounted for.

4.5.1.2 Run R7 (11/17/95) - Battelle Reagent Run at Low Temperature

Run R7 examined the use of the Battelle reagent at substantially lower temperatures (i.e., 190°C and 250°C, 4 hr at each temperature) than used for conventional BCD (i.e., 350°C). Catalyst was added, and the reaction medium used for this run was LW-104 oil. During the course of this run, organic condensate collected in the MTR was successfully recycled back to the reactor. The total condensate collected was 21 g aqueous condensate and 15 mL of organic condensate, with all but 0.6 mL of the organic condensate being recycled back to the reactor. Sampling during this run was problematic. Material was hung up in the sampling probe during sample collection. Analytical results showed that even after 4 hr at 250°C, the material still contained about 10% of the PCB present in the feed. Consequently, the partially treated material was left in the reactor for further treatment in the next run.

4.5.1.3 Run R8 (12/6/95) - Continuation of R7

Since the final product from R7 was not completely treated, R8 was conducted with the same material but at higher temperatures. The STR was operated at 275°C and 285°C for 1 hr at each temperature. Attempts were made to further increase the temperature; however, with the LW-104 medium, increasing the temperature beyond 290°C resulted in the generation of organic condensate refluxing in the glassware below the MTR. During the run, 9 g of aqueous and 22 mL of organic condensate were generated. Nearly all of the organic condensate was returned to the reactor. The material balance calculations showed that 98.6% of the material placed into the reactor was accounted for. After the run, the reactor contents were removed and allowed to settle overnight. Approximately 80% (by volume) of the contents clarified in the form of a recoverable oil.

4.5.1.4 Run R9 (12/12/95) - 50% Reduction of NaOH and Battelle Reagent

The objective of R9 was to reduce the ratio of NaOH and the Battelle reagent to PCB by 50% (relative to R2), and operate for 2 hr at 250°C, 300°C, 350°C. Catalyst was added in this run, and LW-110 oil was used as the reaction medium. No hydrogen donor oil (LW-104) was used. The onset of water collection in the MTR occurred at a reactor temperature of 214°C. During the run, 23 g aqueous condensate and 5.1 mL organic condensate (with 4.1 mL recycled back to reactor) were generated. The material balance calculations showed that 98.2% of the material was accounted for. Analytical results showed that PCB was not adequately destroyed, most likely as a result of underdosage of base.

4.5.2 Process Chemistry

The baseline BCD recipe with the addition of the Battelle reagent was compared with baseline testing (R1, R6). The results from the comparison are provided in Figure 4.8. It should be noted that for R2, the NaOH concentration was half that used in R1 and R6.

It was somewhat unexpected when total PCB levels (Figure 4.8) were reduced to below the treatment target after only 1 hr at 300°C instead of the necessary 2 hr at 350°C for the baseline BCD recipe. Further experimentation on the Battelle reagent indicated that the use of LW-104 may be preferable as the primary matrix because of the lowered operation temperatures. Using LW-104 would have some advantages over the use of LW-110 at a similar cost. First, the use of a lower viscosity oil enables better "settling" separation for splitting the product into sludge and recoverable, reusable oil. Second, in the matrices where a hydrogen donor is required, there would be no need to premix and add both a hydrogen donor and a higher-boiling-point oil medium to successfully treat the matrix. Runs R7, R8, and R9 further explored the use of the Battelle reagent.

As shown in Figure 4.9, in Run R7, 4 hr at 190°C was only effective at reducing 50% of the total PCB content in the reactor, based on an initial PCB content of approximately 15,000 ppm (from a sample taken at 126°C). An additional 4 hr at 250°C resulted in 91% total PCB destruction. R8, which was run to examine higher temperatures for full destruction of the remaining PCB from R7, was intended to operate for 1 hr at 275°C, 300°C, 325°C. The reactor was unable to be heated above 288°C due to the large amount of heat taken up in the reflux of the reactor contents, presumably near the boiling point of LW-104. However, the sample after 1 hr at 275°C showed 99.6% destruction, and the sample after 1 hr at 285°C showed destruction down to the detection limits of the analytical method. From this test, it was surmised (and later shown in Run R12) that operations at 275°C for possibly 2 to 4 hr would suffice for complete destruction using the Battelle reagent with LW-104 as the reaction medium.

It must be appreciated that BCD is not a discrete PCB molecule destruction process, but is actually a series of individual dechlorination reactions that, over the course of the treatment, fully defunctionalize the PCB molecules. To illustrate this, homolog profiles for R7 and R8 were combined to show the dechlorination shift that occurs during treatment. There is a distinct homolog shift as the chlorines are removed and the PCBs are defunctionalized.

In Run R9, the concentrations of the NaOH and the Battelle reagent were reduced to 50% of the loadings used in R2. As shown in Figure 4.10, which compares R9 and R2, the reagent loading reduction resulted in incomplete PCB destruction. Very little destruction occurred after 1 hr at 250°C, indicating that nearly all of the NaOH was consumed.

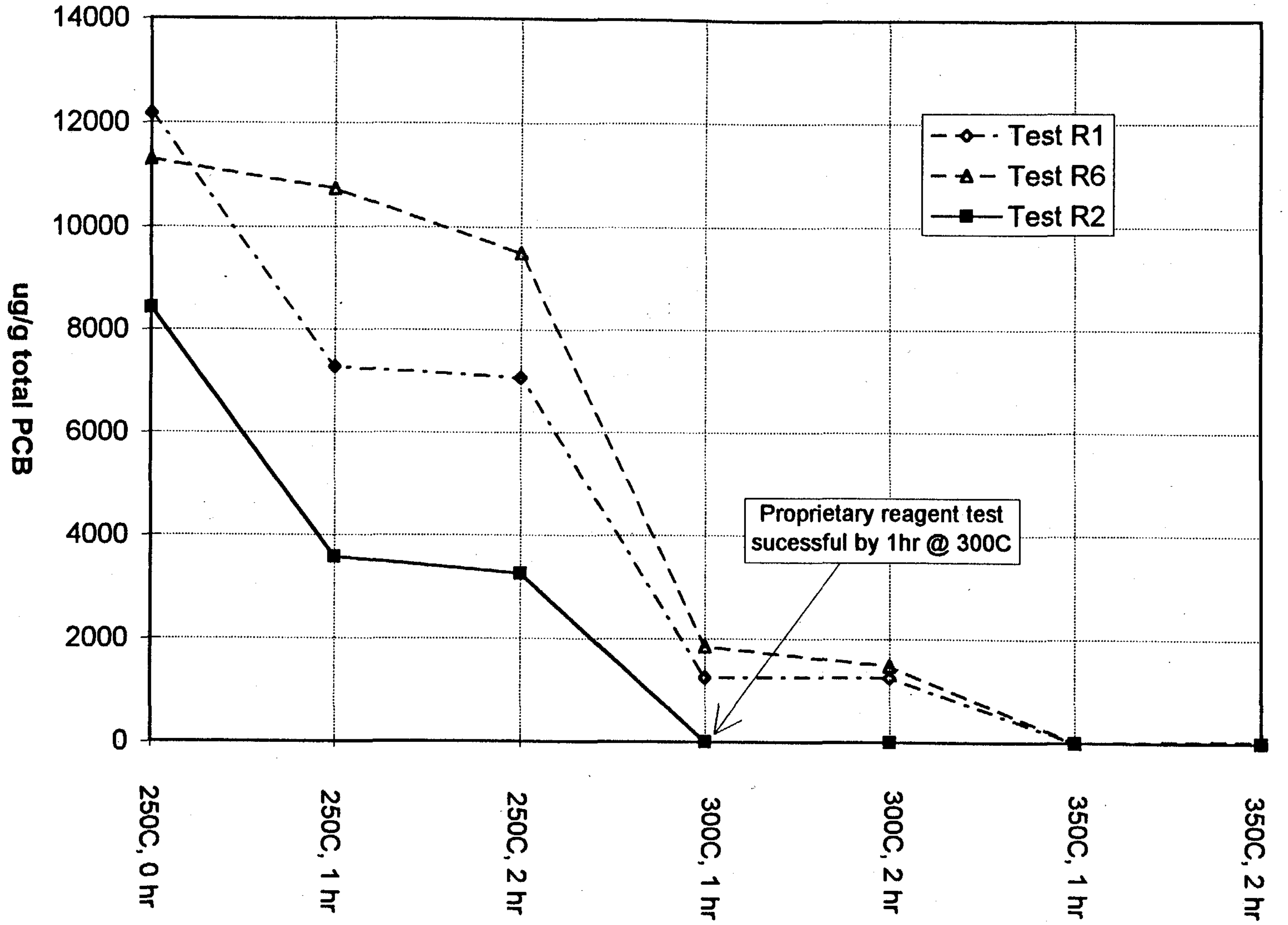


Figure 4.8. Comparison of Battelle Proprietary Reagent Addition to Baseline BCD Testing (R2 vs. R1 and R6)

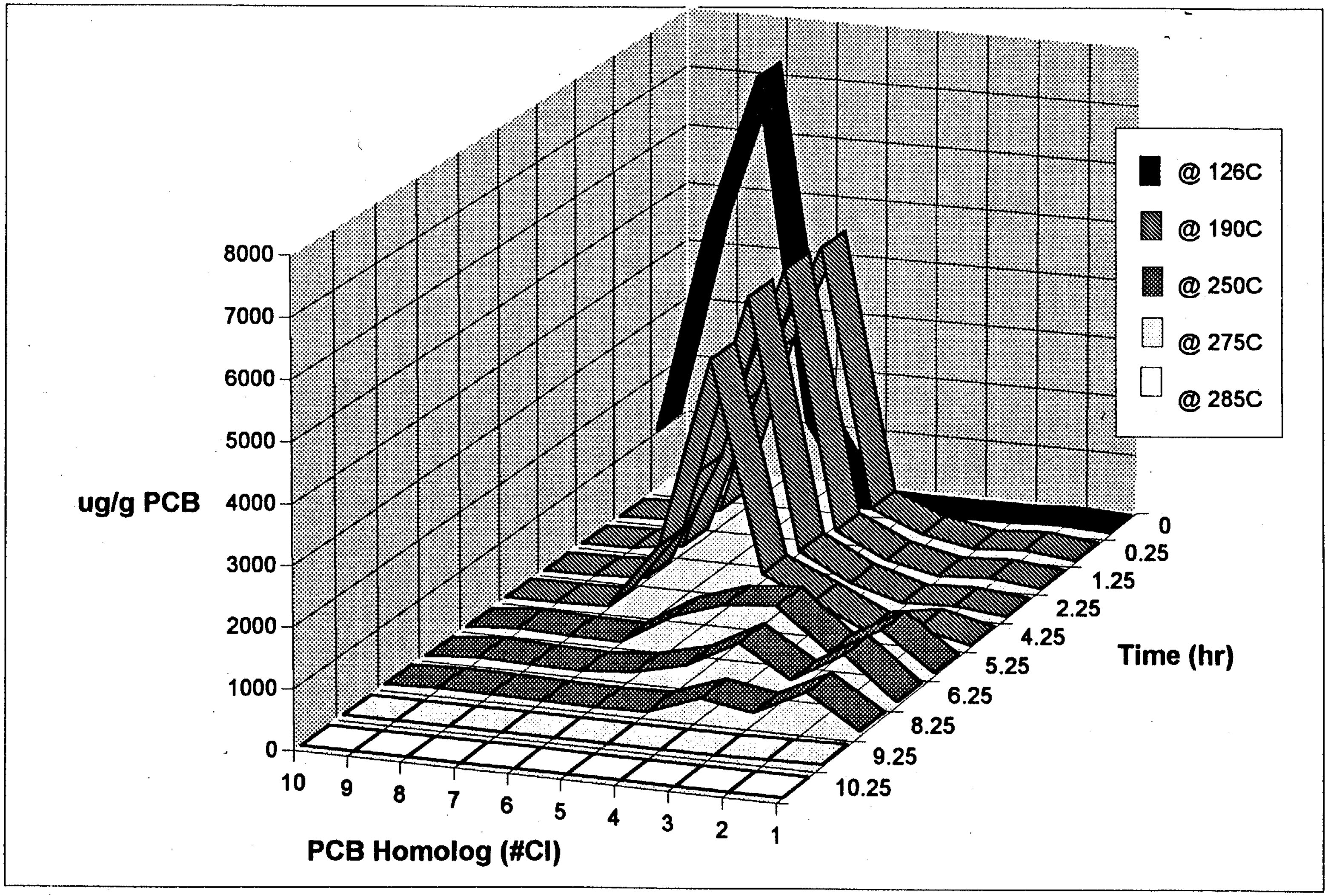


Figure 4.9. PCB Homolog Profile as a Function of Time and Temperature for Runs R7 and R8

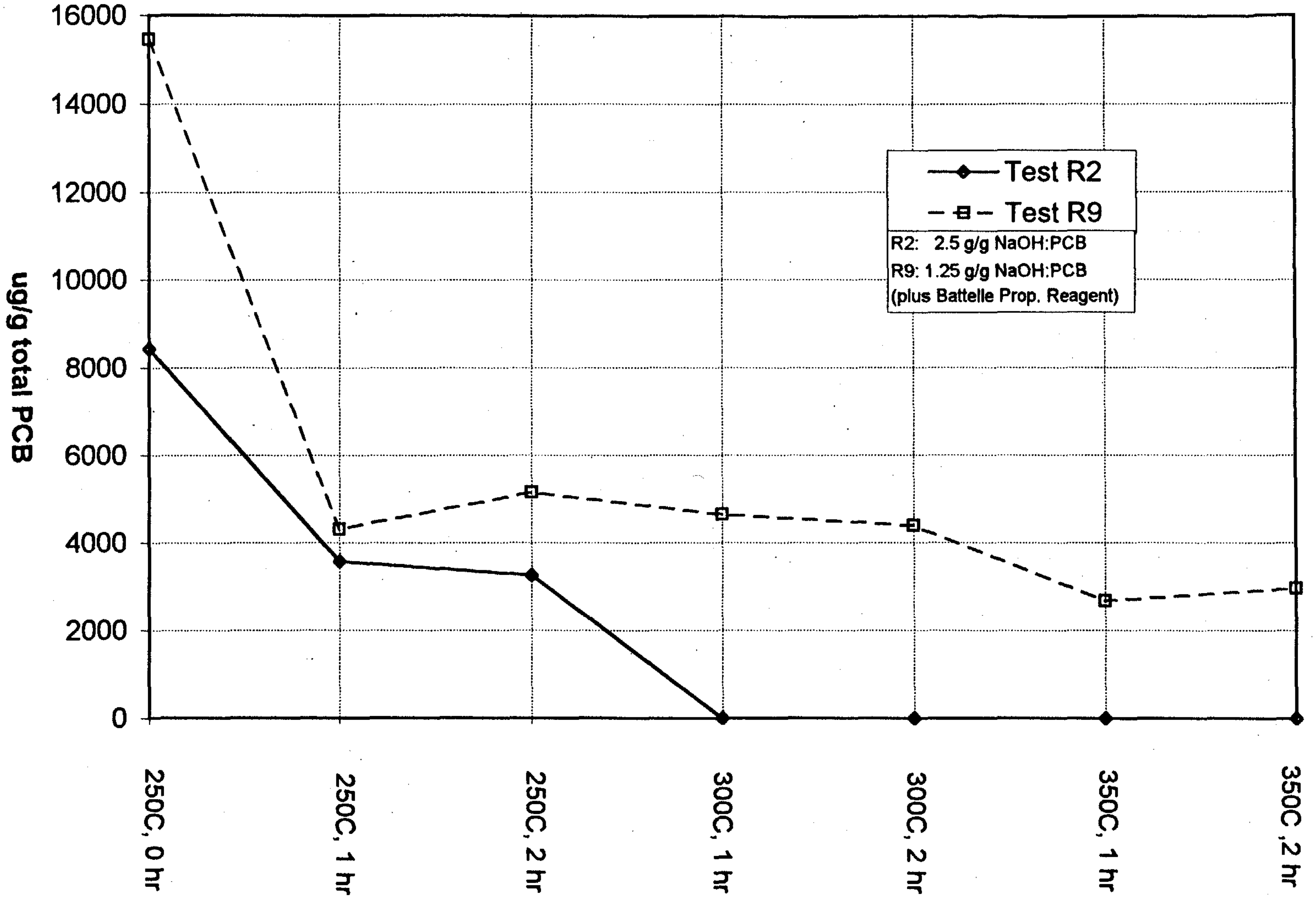


Figure 4.10. Effects of Changing Primary Reagent Loadings (R9 vs. R2)

4.6 High Loading Wool Felt Runs

The high loading wool felt runs were conducted at waste loadings two (2X) and three (3X) times that used in the baseline runs. Operation at higher waste loadings is desirable to enhance the process economics, since the waste loading determines the process throughput for a given reactor size. For the 3X runs, the PCB concentration in the reactor was about 40,000 ppm, and the total solids added to the reactor made up 63% of the total contents. The 3X runs were performed by adding the wool felt and a proportional amount of reagents (NaOH and Battelle reagent) with no compaction. Next, the interstitial spaces between the bulk wool felt pieces were filled with LW-104 oil. This is presumed to be near the maximum loading for this reactor, barring compaction or further wool felt size reduction.

Ways to improve removal of treated material from the reactor were also examined in these runs. For the baseline runs, containing about 13% wool felt, the product from the 2-L STR was removed in most cases by pouring the contents out of the reactor. For the high wool felt runs discussed here, a much more aggressive approach was necessary to remove the treated material, as much of the solids in the reactor tenaciously attached to the bottom and walls of the reactor.

These high loading runs showed that the ratio of oil to wool felt is an important parameter for predicting the difficulties associated with removing the treated contents. In the baseline runs, the oil to wool felt ratios were approximately 6:1. In contrast, for the 3X loading runs, the oil to wool felt ratio was about 1.3:1.

Results from this testing are provided in Table 4.3. These results indicated that removing a treated product from large-scale systems is likely to be problematic. With the wool felt containing approximately 14% by weight PCB, testing showed that the reagent loading (relative to the baseline runs) could be reduced by 33%. Testing indicated that at 50% of the baseline loadings, complete dechlorination of the PCB was not achieved.

4.6.1 Run Summaries

4.6.1.1 Run R10 (12/15/95) - 3X Wool Felt Loading, Baseline NaOH and Battelle Reagent Addition

The objectives of R10 were to simulate a potential pilot-scale run with the Battelle reagent at 3X the baseline wool felt loading and to examine post-run materials handling behavior. No catalyst was used. LW-104 was used as the reaction medium and was added at mass ratio to wool felt of 1.3:1. The total reactor contents weighed 1472 g and included 429 g of wool felt.

For this run, wool felt pieces of approximately 2 x 2 x 1 cm were used. The agitator was engaged when the temperature in the reactor reached approximately 165°C. Engagement of the agitator at a lower temperature resulted in vibration and shaking of the system as the impeller collided with the wool felt pieces. This compares with approximately 90°C for an agitator engagement temperature with the baseline loading of wool felt. Water began to come off at 165°C. Operations were essentially

Table 4.3. Summary of High Loading Wool Felt Runs

Run No.	Run Conditions (Temp., Time)	Successfully Treated (yes/no), Uncorrected[a] PCB Concentration, ppm	Wool Felt (g)	Est. PCB (g)	Reagent Loadings					
					LW-110 (g)	LW-104 (g)	Other (g)	NaOH (g)	Catalyst (g)	Battelle Proprietary Reagent (y/n)
R10	 250°C, 2 hr 275°C, 2 hr 285°C, 1 hr	Feed 38,000 No, 120 Yes, 11 Yes, 14	429	60	None	548	None	191	None	Yes
R12	 275°C, 1 hr 275°C, 2 hr 275°C, 3 hr 275°C, 4 hr	Feed 32,000 Yes, 6 Yes, 7 Yes, 4 Yes, 6	431	60	None	550	None	143	None	Yes
R-14	 275°C, 1 hr 275°C, 2 hr 275°C, 3 hr 275°C, 4 hr	Feed 27,000 No, 220 Yes, 13 Yes, 6 Yes, 13	287	40	None	856	None	85	None	Yes
R-16	 275°C, 1 hr 275°C, 2 hr 275°C, 3 hr 275°C, 4 hr	Feed 28,000 No, 1100 No, 650 No, 340 No, 200	286	40	None	857	Yes, BCD Group Reagent, 25	64	None	Yes
R-18	 275°C, 1 hr 275°C, 2 hr 275°, 3 hr 275°C, 4 hr	Feed 32,000 No, 20 Yes, 2 Yes, 3 Yes, 3	410	57	None	533	Yes, BCD Group Reagent, 25	122	None	Yes

(a) Interference and contamination have not been subtracted out.

uneventful, with the exception of a possible exothermic reaction at 275°C. At this temperature, it appeared that minimal heat input was necessary to keep the reactor at temperature. Recycle of organic condensate went smoothly. During the run, 90 g of aqueous condensate and 66 g of organic condensate were generated. All but 1 mL of the organic condensate was returned to the reactor.

Following R10, the reactor was left sealed for a period of about 3 weeks, due to analytical constraints, and the contents were allowed to settle. Upon disassembly of the reactor, the contents were found to have separated very cleanly, with the light oil phase on top, and the solids hardened into a solid mass at the bottom of the reactor. To clean the reactor, the solids had to be chipped out with a chisel.

4.6.1.2 Run R12 (2/22/96) - 3X Loading, 75% NaOH and Battelle Reagent Addition

The objectives of R12 were to perform another 3X wool felt loading run, reduce the NaOH and Battelle reagent loading by 25%, and examine the merits of removing the treated contents immediately following the run while still at an elevated temperature. For this run, the reactor was held at 275°C for 4 hr. No catalyst was used, and LW-104 was used as the reaction medium. Total condensate generation was 71 g aqueous and 93 mL organic, with essentially all organic condensate being recycled back to the reactor. During cooldown, the agitator remained on. The reactor contents were removed while still hot (just over 100°C). However, even at the elevated temperature, solid residual remaining in the reactor had to be removed by chipping. Although the quantity of solid residual requiring chipping-out was significantly less than for R10, it was still enough to create potential problems in larger-scale reactor systems. Aggressive solid residual removal options will likely be limited in larger-scale reactor systems.

4.6.1.3 Run R14 (3/14/96) - 2X Loading, 66% NaOH and Battelle Reagent Addition

The objective of this run was to simulate a potential pilot-scale run with a 2X wool felt loading and further reduce the reagent loading (NaOH and Battelle reagent) to 66% of that used in R10, and to examine post-run materials handling. For R14, the oil (LW-104) to wool felt mass ratio was 3:1. This run was conducted at 275°C for 4 hr. The agitator was engaged when the temperature in the reactor reached approximately 90°C. This compares with approximately 190°C for an agitator engagement temperature for R10 and R12, most likely due to lower solids content. The condensate was 53.1 g aqueous and 1 g organic (46.7 mL organic total, with 45.7 being recycled during the course of run). From the material balance calculations, 98.8% of the material added to the reactor was accounted for.

After holding for 4 hr at 275°C the heat was turned off, and the system was left with the agitator on for 12 hr. While reactor cleanout was easier for this run than in R10 and R12, some material adhered to the sides and bottom of the reactor and had to be removed with a hard scraper. The material around and above the stirrer remained fluid (with resuspendable small particulates of hard solid). While operation of a larger-scale system would be possible under these conditions, after several runs, it is most likely manual cleanout of the reactor would be required. Stirring during cooldown appears to be beneficial; however, it does not solve all adhesion problems. Use of a rake at the bottom of a reactor may improve the manner in which the solids appear to agglomerate.

4.6.1.4 Run R16 (3/28/96) - 2X Wool Felt Loading, 66% NaOH and Battelle Reagent, BCD Group Reagent

This run was similar to R14 where 2X loaded wool felt was treated, but included the BCD Group, Inc., proprietary reagent, which is reported to act as an inhibitor to the formation of the hard, solidified residual that is characteristic of many of the heavily loaded BCD tests. This run was conducted with an NaOH and Battelle reagent loading at 50% of that used in R10. During R16, 42.2 g aqueous condensate and 33 mL of oil were collected, with all but 0.15 mL being recycled. The quantity of aqueous condensate was approximately 17% less that what was collected in the nearly identical run, R14. However, for this test, it is important to note the matrix itself contained less water at a result of the lower reagent and wool felt addition rates (as compared with R10). Organic condensate collection was down by about 30%. The BCD Group reagent was reported to have the added benefit of keeping water within the matrix, which minimizes the potential for steam stripping of PCB. The material balance calculations showed 98.1% of the material added to the reactor was accounted for.

At the conclusion of R16, the reactor was allowed to cool and was under agitation for approximately 12 hr. Upon system disassembly, it was observed that the character of the residuals in the reactor was very different than found during previous tests of this type, including R14. The solids at the bottom of the reactor had not solidified into a hard, crystalline mass but formed a heavy slurry that contained very small granules and was nearly flowable after vigorous agitation at room temperature. There was no solid mass attached to the reactor walls, and the material poured out of the reactor but was difficult to flow through a 1-cm funnel neck. With vigorous agitation and a slightly elevated temperature, it may be possible to pump the residual out of a reactor vessel in this condition.

From a materials handling perspective, R16 can be considered successful. While there still is a solid residual that needs to be addressed at the conclusion of treatment, the BCD Group reagent appears to yield a slurry that is pumpable, eliminating the need for an elaborate reactor that can handle hard, crystalline solids. However, at the reagent dosages used for this run, the PCB concentration was not reduced to the target treatment standard. At higher reagent loadings, the BCD Group reagent may not be as effective.

4.6.1.5 Run R18 (4/26/96) - 3X Wool Felt Loading, 66% NaOH and Battelle Reagent, BCD Group Reagent

The objective of this run was to simulate a potential pilot-scale run at 3X the baseline wool felt loading with 66% of the NaOH and Battelle reagent (relative to R10) and examine the effects of the BCD Group reagent at the higher loadings. Run R18 was a repeat of R16, except with a higher loading of wool felt and reagents. During the run at about 218°C, significant condensate generation occurred, and the pressure relief line was bubbling rapidly. The condenser overfilled with condensate, resulting in slugging through the condenser for several minutes. Approximately 20 mL of material were carried out of the reactor and into the knockout pot. During the run, approximately 58 g of aqueous and 65 mL of organic condensate were collected in the MTR. All but 1 mL of the organic condensate was recycled back to the reactor. The material balance calculations showed approximately 99% of the material loaded into the reactor was accounted for.

Data on condensate generation from the 3X wool felt loading runs are provided in Table 4.4. These data show that these runs produced similar quantities of condensate, and that the reagent loading appears to affect the aqueous condensate generation.

After the run, heat was shut off, and the reactor allowed to cool with the stirrer engaged. After cooling, the agitator seized. Upon disassembly, some phenolic odor was present but made up only part of the odor. The reactor contents separated cleanly into distinct solid and oil phases. The stirshaft was easily removed from the reactor and appeared mostly to be bound up from rotation, rather than solidified into the solid reactor product phase. Much of the solid phase was then broken up by crushing and mixing it by hand using the agitator shaft. This suspended an estimated 60% to 70% of the solids to a form that was easily pourable with the bulk of the oil. The slurry was then poured out and had to be physically assisted through a 1-cm neck funnel.

The remainder of the hardened solids (a cake approximately 1-cm thick) took the form of a hard crystalline material similar to what was retrieved from previous high wool felt loadings. The material was removed via impaction with a plastic spatula and had the shiny crystalline face against the steel reactor that was characteristic of R10 when none of the BCD Group reagent was added. For this test, the BCD Group reagent was only partially effective in eliminating the product handling difficulties. Upon settling, approximately 50% of the reactor contents clarified after approximately 1 week. Eighty-seven percent of the oil added to the reactor (as the reaction medium) was recovered for potential reuse, using settling and decanting as the only separation mechanism.

4.6.2 Process Chemistry

A baseline loading of NaOH and Battelle reagent was added at ratios of 3.2 g NaOH and 5.2 g of Battelle reagent per gram of PCB (or 0.45 g NaOH and 0.73 g of Battelle reagent per gram of wool felt). These ratios were successfully demonstrated in Runs R2, R8, and R10. To simplify testing, both reagents in this baseline were scaled equivalently in subsequent tests. Thus, in the following discussions, 75% reagent loading refers to 75% of the baseline of both the NaOH and the Battelle reagent.

It was surmised that the higher ratio of wool felt to oil should not significantly affect the process chemistry unless the reaction rates were limited by diffusion of the PCB from the wool felt to the bulk oil medium. Comparison of R2 (loaded with 140 g wool felt) with R10 (loaded with 430 g wool felt) showed that complete dechlorination was achieved after 1 hr at 300°C for R2 and between 1 hr to 2 hr at 275°C for R10.

Table 4.4. Condensate Generation Parameters

Parameter	R10	R12	R18
Total Feed Mass (g)	1472.7	1352.5	1287.4
NaOH and Battelle Reagent	100%	75%	66%
BCD Group Reagent:NaOH	0	0	20%
Total Aqueous Condensate (g)	90	70.5	58
Total Organic Condensate Generated (accumulated) mL	67 (1)	93 (0.1)	66 (1)
Total Condensate as % Feed	11%	12%	9.6%

4.6.2.1 Reagent Minimization

Adjustment of the baseline loading yielded some success in reducing the expected loading for successful PCB treatment in this matrix. In these tests, the reactor was brought to 275°C and held for up to 4 hr, with samples usually being taken at each hour at temperature. Tests subsequent to R10 were performed at 74%, 66%, and 50% by weight of the baseline loading, and the total measured PCB vs. time is plotted for these runs in Figure 4.11.

While the ratios of reagent to wool felt feedstock were strictly controlled for the runs in Figure 4.11, the total amount of wool felt, and thus the ratio of wool felt to oil media in four tests was not equivalent. Runs R14 and R16 were both loaded with about 290 g of wool felt with a 1:3 weight ratio of wool felt to oil. Runs R12 and R18 were both loaded with approximately 430 g of wool felt with a weight ratio of 1:1.3 of wool felt to oil. In addition, R16 and R18 were each spiked with 25 g of the BCD Group reagent. This reagent was designed to yield a more manageable product from the process. However, comparing R14 to R18, both at 66% of baseline reagent loading, there appears to be only a slight effect on the destruction PCB efficiency, which could potentially be attributed to the difference in the oil/wool felt ratios or the addition of the BCD Group reagent.

Within 1 hr at 275°C and 75% reagent loading in R12, the PCB content in the reactor was reduced to below detection limits (Figure 4.11). This test was considered a success, and further reagent loading reduction was attempted.

At 66% reagent loading, for both R14 and R18, after 2 hr at 275°C the PCB in the reactor was reduced to the analytical detection limits (Figure 4.11). In the 1-hr samples, PCB concentrations were 220 ppm in R14 and 20 ppm in R18. The PCB homolog profile for the 1-hr sample for R14 was 95 ppm 1-CB and 112 ppm 2-CB, and the balance was 3- to 8-CB. The 1-hr sample for R18 contained 16 ppm 1-CB, 3 ppm 2-CB, and less than 0.5 ppm each of 4-CB, 5-CB, and 7-CB. There are several possible explanations for the minor discrepancies in the PCB concentrations in the 1-hr samples from the two 66% reagent loaded runs. First, there could be some minor effect from the difference in oil/wool felt ratios or from the BCD Group reagent as explained above. Also, R18 was loaded with

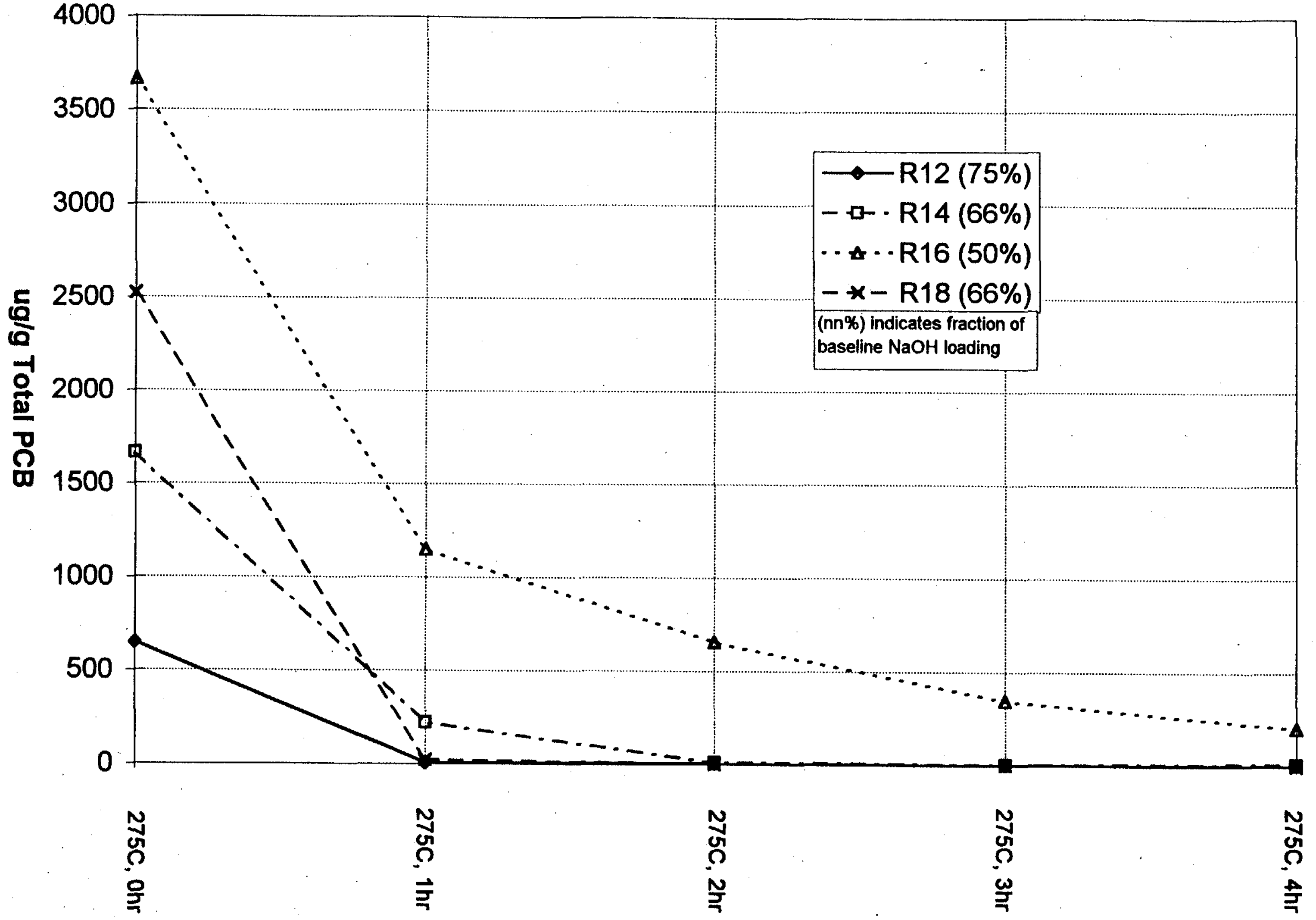


Figure 4.11. Effects of Reagent Loading on Total PCB (Runs R12, R14, R16 and R18)

50% more NaOH than R14 (since there was 50% more wool felt in R18), and the NaOH may be partially catalytic in the BCD reaction, due to the possibility that a constant amount is consumed by a volume of oil regardless of feedstock loading.

While the 50% reagent loading in R16 was successful in destroying 99.2% of the PCB in the reactor after 4 hr at 275°C, the matrix in the reactor still contained approximately 200 ppm PCB. The homolog profile for the 4-hr sample of R16 is 119 ppm 1-CB, 79 ppm 2-CB, and the balance made up of 3- to 8-CB homologs.

Based on the results shown in Figure 4.11, the 50% reagent loading was insufficient for complete destruction of PCB in a wool felt matrix. Consequently, the 66% baseline reagent loading was selected as the most probable recipe for operations with wool felt treatment in the pilot-scale system.

4.6.2.2 BCD Group Proprietary Reagent

While the solids handling part of R16 was a success, the actual treatment of the PCB had not been complete. This was attributed to the low NaOH loading (50% baseline reagent test). The second test of this reagent was scheduled to ensure that the reagent was not responsible for the failure of the run.

R18 was conducted as a verification test of the BCD group reagent, using the 66% baseline reagent loading, which had proven to be effective in R14. The reagent loading was cut in half with respect to weight ratio to the NaOH to determine if the product crystallization could be prevented with lower dosage. The consistency of the reactor contents after the run indicated that the reagent dosage was too low to achieve full granularization of the product. However, upon analysis, the timed samples showed that all of the PCB was treated in the reactor after 2 hr at 275°C, similar to what was found in the R14, which was loaded similarly with the exception that it contained no BCD Group reagent.

4.7 Paint Chip Runs

In addition to the wool felt tests, Stage 2 tests were run with the paint chips collected from paint removal operations including scraping and use of needle guns, but not associated with shot blasting. Analytical results showed that the paint chips received contain between 500 and 600 ppm PCB. That is, each kilogram of paint chips contains only about 0.5 g PCB. Despite the relatively low PCB concentration, the disposal cost for paint chips approaches that of wool felt.

An examination of the physical behavior of the paint chips in the heated oil medium determined that, in the absence of other reagents (e.g., NaOH), the paint chips maintained their size and shape in oil heated to 300°C. However, the paint chips darkened, and the oil discolored. The chips settled out, and the oil clarified following the testing. Once sufficient quantities of reagents were added, specifically NaOH, and the reactor contents heated to 350°C, the paint chips underwent significant physical degradation. These observations, along with the results from R15, indicate that reactions with the paint chip matrix likely consume NaOH.

The run conditions and results from the testing with paint chips are summarized in Table 4.5. The results show that very high waste loadings are achievable, and that the treated product can be readily removed from the reactor. The treated product is a thick, homogeneous slurry, with little or no separable oil (i.e., little or no oil can be recycled for use in subsequent runs). Although the PCB concentration in the paint chips is low, it appears that to effect adequate treatment, NaOH must be added at a ratio approximately 100 times greater than the standard BCD NaOH:PCB mass ratio of 2.5:1.

4.7.1 Run Summaries

4.7.1.1 Run R15 (3/22/96) - Initial Paint Chip Run

The objective of this test was to perform a run similar to the baseline run (R1) with paint chip feed. The run was conducted for 2 hr at 250°C, 300°C, 350°C. Paint chip loading was 203 g, which gave a PCB content in the reactor of 0.12 g. Although the actual PCB concentration in the paint chips is between 500 and 600 ppm, a concentration of 5000 ppm was used for determining reagent loadings for this run to provide additional base that may be consumed/tied up by the paint chip matrix.

Initial heatup was performed more aggressively due to the expected lack of bulk water in the reactor. Condensate formation appeared at around 130°C. By the end of the run, the silicon offgas line between the condenser and impingement tube turned a red-orange, and the line between the impinger and carbon bed line turned pink. It is suspected that pigmentation in the paint chips was responsible for the colors within the offgas system. Condensate generation in R15 was substantially less than for similar wool felt runs. Total condensate collected was 12.4 g aqueous and 5.8 mL organic, with 4.2 mL being recycled. From the material balance calculations, approximately 98.1% of the material added to the reactor was accounted for.

Upon disassembly, it was noted that the paint chips were still in a free solid phase and similar in consistency to the original feed, although the solid residual appeared to be blackened and possibly of smaller particle size. No apparent caking or solidifying of the reactor solids was visible; however it must be noted that the total concentration of NaOH in the reactor was very small in comparison to wool felt experiments.

4.7.1.2 Run R17 (4/9/96) - High Loading Paint Chips, Increased Reagent Loading

The main objective of R17 was to determine if lack of success in R15 was due to consumption/tie up of NaOH in the matrix; the ratio of NaOH:PCB was increased by a factor of 20. A second objective was to examine operability and post-run materials handling aspects associated with a high paint chip loading. For this run, 400 g of paint chips were added, and a ratio of 1.3:1 oil to paint chips was used. PCB was successfully reduced from approximately 330 ppm to less than 2 ppm per congener after 2 hr at 300°C.

Table 4.5. Summary of Paint Chip Runs

Run No.	Run Conditions (Temp., Time)	Successfully Treated (yes/no/AE[a]), Uncorrected[b] PCB Concentration, ppm	Paint Chips (g)	Est. PCB (g)	Reagent Loadings					
					LW-110 (g)	LW-104 (g)	Other (g)	NaOH (g)	Catalyst (g)	Battelle Proprietary Reagent (y/n)
R15		Feed 160	203	0.12	800	2.5	None	2.5	7.5	No
	250°C, 2 hr	No, 140								
	300°C, 2 hr	No, 130								
	350°C, 2 hr	No, 110								
R17		Feed 330	400	0.23	518	10	None	100	7.5	No
	300°C, 2 hr	Yes, 6								
	350°C, 2 hr	Yes, 2								
R19		Feed 460	425	0.24	0	518	None	27	None	Yes
	275°C, 1 hr	No, 250								
	275°C, 2 hr	No, 180								
	275°C, 3 hr	No, 240								
	275°C, 4 hr	No, 230								
R20		Feed 480	601	0.34	601	0	None	60	None	Yes
	275°C, 1 hr	No, AE								
	275°C, 2 hr	No, AE								
	275°C, 3 hr	No, AE								
	275°C, 4 hr	No, AE								

(a) AE analytical error, data not reportable.
(b) Interference and contamination have not been subtracted out

Condensate generation included 38.2 mL aqueous and 12 mL organic, with 11 mL being recycled. The material balance calculations showed that 98.9% of the material added to the reactor was accounted for. Discoloration of the offgas tubing was less pronounced in R17 than in R15.

Upon completion of the run, there was very little free liquid upon opening the reactor. The liquid that did exist was located around the agitator. The product stream was nearly homogeneous, similar to applesauce in consistency. Some clumps were present. Very little of the material adhered to the reactor vessel walls, and although thick, the material was pourable (and pumpable). After completion of this run, attempts were made to polymerize the treated product to create a solid final waste form. Various concentrations of elemental sulfur and zinc oxide were added prior to heating the mixtures. These attempts were unsuccessful, presumably as a result a lack of olefinic constituents in the matrix.

4.7.1.3 Run R19 (5/22/96) - High Loading Paint Chips, Battelle Reagent

Run R19 was performed to determine if the conditions used for the successful high paint chip loading run (R17) could be optimized. Optimization goals included reducing the NaOH loading to about 25% of R17, reducing the reaction temperature by using the Battelle reagent, and eliminating catalyst. The run was conducted at 275°C for 4 hr.

For this run, 426 g paint chips were loaded into the reactor. Approximately 4% of the total matrix mass (36 g) came off as aqueous condensate, and less than 2% (17 mL) of the matrix mass came off as organic condensate. The material balance calculations showed that 98.1% of the material was accounted for.

There was very little free liquid upon opening the reactor. The residual paint chips were less degraded in this run than in R17. Upon disassembly, the contents were manually agitated and were poured out of the reactor. Some clumps were present. The material was not physically cemented to the reactor vessel walls after being manually agitated. After settling for 1 week, less than 5% of the reactor contents clarified into a recoverable oil.

4.7.1.4 Run R20 (8/9/96) - High Loading Paint Chips, Battelle Reagent, Higher Reagent Loadings

The objectives of this run were to increase paint chip loading to approximately 50% (oil:paint chips = 1:1); adjust the base loading to a level between that of R17 and R19; use LW-110 as the reaction medium; and eliminate catalyst and the donor oil since the latex in the paint chips should provide sufficient donor material. This run was conducted for 4 hr at 275°C. A total of 601.4 g of paint chips were added.

The agitator could not be engaged until a temperature of 123°C was achieved. Heavy aqueous condensate began to come off at 123°C. For the run, 61 g aqueous condensate and 6 mL of organic condensate were collected. The material balance calculations accounted for 99.6%.

Upon completion of the run, the contents were allowed to cool while agitating. The treated product resembled thick applesauce. All of the contents of the reactor were easily removed with none adhering to the vessel walls. After a sample of the treated material was centrifuged for 30 min, approximately 7% of the material separated into a clarified oil. Based on this run, it is likely that the waste loading can be increased even further. Although the analytical results from this run are not reportable (due to peak smearing from interferences), the results indicated that significant PCB remained even after 4 hr at 275°C.

4.7.2 Process Chemistry

Total PCB in a paint chip feed is high with respect to allowable regulatory limits; however, it is relatively small in comparison to the concentration in the wool felt matrix. Notably, this means that the paint is a much larger constituent of the treatment matrix, and that competitive consumption of the NaOH by the paint is much more of an issue than for the wool felt. Under standard BCD loading conditions (2.5 g NaOH per g of PCB), the small amount of base added is quickly consumed by the paint chip matrix and none is left for the reaction. This behavior was demonstrated in R15, in which the standard loading was used[a] for the test (2.5 g NaOH per gram of PCB), and appeared to have no effect on PCB concentration after 2 hr at each of 250°C and 300°C; and achieved only about 13% destruction after 2 hr at 350°C. For R17, the PCB concentration was reduced from 330 ppm to 17 ppm while the reactor heated from room temperature to 300°C. After 2 hr at 300°C, the PCB concentration was reduced to below 2 ppm per congener.

For R19, in which the NaOH to PCB ratio was reduced by a factor of 4 and the run conducted at a temperature of 275°C for 4 hr, the PCB concentration was only reduced by about 50% after 4 hr at 275°C. The degree of chlorination was decreased from an average of 5.6 in the feed to 2.6 chlorines per PCB molecule in the final treated product.

Run R20 was performed with a higher loading of paint chips and a NaOH to PCB ratio 55% greater than R19 and 40% of that used for the successful run, R17. Unfortunately, PCB was not successfully treated during this run.

4.8 Other Runs

Several miscellaneous runs were conducted to examine BCD processing alternatives, such as aqueous-phase BCD, and BCD Stage 1 treatment for wool felt and for paint chip waste associated with shot blast removal.

(a) Assuming 5000 ppm in the paint chips; however, actual PCB concentration was approximately 600 ppm.

4.8.1 Run R11 (1/22&23/96) - Closed-system BCD in Aqueous Medium

Potential benefits may be derived from conducting the BCD process in a closed aqueous-phase system. Through the use of a closed system, generated offgases are maintained at temperature for sufficient operating time to effect complete dechlorination. With an aqueous-phase system, better separation between the solids and the reaction medium (water) may be possible, which could reduce the volume of secondary wastes.

The objectives of R11 were to conduct a closed-system hydrothermal BCD run with no donor and no catalyst and to determine if base solubility is a major factor on the BCD reactions. In an aqueous system, NaOH is very soluble; however, the PCB solubility is very limited until supercritical-type conditions are approached. This run was conducted for 2 hr at 250°C, 90 min at 300°C, and 2 hr at 350°C. The material balance calculations showed 93% of the material was accounted for. Material that stuck to the agitator and in the head of the reactor could not be measured.

Overall, this run went extremely well from a reactor operations perspective. After completion of the run, the contents were drained from the reactor and allow to settle overnight. Approximately 90% to 95% of the contents clarified. Solids at the bottom appeared to be fine dust (degraded wool). The particulate phase was easy to resuspend. Wool felt appeared to fall apart, and a homogeneous mixture resulted in an aqueous medium.

The analytical results showed that the PCB concentration was reduced from approximately 18,000 ppm to about 150 ppm after 2 hr at 350°C. The congener makeup of the remaining PCB was shifted downwards. To achieve the target treatment criterion of 2 ppm per congener, modification of the process chemistry would likely be required. Since the oil-phase BCD treatment was so successful in achieving the target treatment criterion, no further closed-system, aqueous-phase testing was conducted.

4.8.2 Run R13 (3/8/96) - BCD Stage 1 on Wool Felt

Because of the operational difficulties associated with treating high loadings of wool felt, a test was conducted to examine the feasibility of performing BCD Stage 1 to remove PCB from the wool felt matrix. In BCD Stage 1 operations, solid waste is mixed with a catalyst and heated to approximately 350°C for 1 hr to destroy and desorb PCBs. The desorbed PCBs are then treated in Stage 2 of the BCD process (i.e., liquid-phase BCD).

In this run, 100 g of wool felt pieces of approximately 2 x 2 x 1 cm were placed into the reactor. Next, sodium bicarbonate was added (15% by weight), and the reactor contents shaken. The reactor was opened, and visual examination verified that all of the wool felt pieces had been coated with sodium bicarbonate. Excess sodium bicarbonate was present at the bottom of the reactor. The reactor was heated to 350°C, and the vapors were swept with a nitrogen purge. At about 15 min into the target temperature (350°C), a white precipitate with a waxy consistency was observed to be forming in the condenser. Solids appeared to condense out in the offgas line (MTR and condenser). For much of the run, the MTR was held at above 330°C. [In a large-scale process, this material condensing out could cause blockage to the offgas line and fouling of the offgas cleaning equipment.] Later it was noted that this precipitate exhibited a phenol-like odor. During the run, a total of 9 g of aqueous condensate and 3 mL of organic condensate were collected. Even though the offgas was polished through a carbon bed, the system still emitted an unpleasant order (similar to burning hair). Upon completion of operations, the reactor was opened and the material remaining can be described as black, amorphous tar, similar in appearance to cooked asphalt. This material could create materials handling difficulties in a scaled-up system.

The treatment only removed about 50% of the PCB from the wool felt; however, a significant downward homolog shift was observed in the residual wool felt. If Stage 1 BCD is to be used to treat wool felt, a carrier solvent will likely be required. However, due to time limitations, and problems encountered during the test, Stage 1 BCD testing with wool felt was not pursued further.

4.8.3 Run R21 (8/21/96) - BCD Stage 1 Treatment of Paint Chips

Paint chip waste obtained from PSNSY in August 1996 for use in the 20-gal STR differed significantly from the batch of paint chips obtained for the bench-scale testing. The material used for the bench-scale testing was generated primarily from paint removal operations with a needle gun and contained essentially 100% paint chips (i.e., contained little or no debris). In contrast, the material obtained for the pilot-scale testing was obtained from the dust/debris collection system associated with shot/sand blasting. In addition to paint chips, the material contained metal fines, spent blasting sand, wood, plastic, and other miscellaneous debris. From visual inspections, paint chips made up less than half the mass of this material. Due to the high inorganic solids content, the material appeared to be an appropriate candidate for treatment via Stage 1 of the BCD process.

The objectives of this test was to perform BCD Stage 1 treatment on shot/sand blast debris, and compare the results to unassisted thermal desorption and a proprietary desorption process. For the test, the bottom of the 2-L STR was filled with gravel, and three crucibles containing paint chips and reagents were inserted into the gravel bed. Each crucible contained approximately 30 g of paint chips, which filled the crucibles to a depth of about 3 cm. The first crucible contained paint chips with no additives; the second contained paint chips to which 10% by weight sodium bicarbonate had been added (i.e., baseline Stage 1 BCD); and the third contained paint chips and a desorption additive, also loaded at 10% by weight. For both crucibles containing reagents, intimate mixing of the reagents with the paint chips had been performed.

The paint chips were heated to 350°C and held there for 1 hr. However, during the run, the temperature climbed to approximately 370°C for about 10 min. A nitrogen purge was maintained over the reactor to sweep the system and to ensure the exclusion of air. During the run, aqueous condensate generation was initiated at a bed temperature of 100°C. While at the hold temperature, smoke was visible in the offgas line. A small quantity of smoke was able to penetrate through the GAC bed. A total of 6.5 g of aqueous condensate and 1.5 mL of organic condensate were generated. The organic condensate exhibited a distinct phenol odor. From the material balance calculations, 99.7% of the material was accounted for.

After completion of the run, the crucibles were removed from the reactor and reweighed. The paint chips containing no reagent lost 6.9% of its mass. These paint chips had darkened and were sticky with some agglomeration on the crucible wall. The paint chips to which the 10% by weight sodium bicarbonate had been added lost 9.4% of their mass. These paint chips were easily removed from the crucible. The paint chips treated with 10% by weight of the desorption additive lost 8.4% of their mass and had undergone very little physical change.

Analytical results showed that the PCB concentration in all three crucibles was reduced from approximately 260 ppm PCB to less than 2 ppm total. With sodium bicarbonate addition, the final concentration was 0.034 ppm, compared to 0.12 with no chemical addition. The paint chips that were mixed with the desorption additive had a final PCB concentration between 1 and 2 ppm. These results suggest that BCD Stage 1 and unassisted thermal desorption are potentially viable methods for treatment of paint chips/debris from PSNSY.

5.0 Pilot-scale Testing in the 20-gal STR

The pilot-scale testing in the 20-gal STR was conducted to confirm the bench-scale results in a near-production size system and to examine large-scale system operability. Conditions used in the 20-gal STR duplicated conditions previously examined in the 2-L STR.

In June 1996, the pilot-scale reactor system (described in Section 5.1) was completely assembled and then tested with water and oil. Additionally, three pilot-scale runs were conducted using wool felt as the PCB-containing feedstock. In August, a fourth run was conducted using a 50/50 blend of wool felt and paint chips as the feedstock. The following sections include a description of the pilot-scale system equipment; operating strategies; and summaries of the runs.

5.1 Equipment Description

The design of the pilot-scale STR system was based on experience gained both from testing with the 2-L bench-scale STR and from the design and operation of the 400-gal STR in Guam. Table 5.1 describes the major components associated with the 20-gal pilot-scale STR.

The STR is a 304 stainless steel tank, 18 in. (46 cm) in diameter and 22 in. (56 cm) high, that was designed to operate up to 400°C at up to 5 psig. As a safety precaution, there are no penetrations in the walls or bottom of the STR. All ports are located on the lid of the vessel. The 20-gal STR system is depicted in Figure 5.1.

The STR was sized to treat approximately 12 gal (45 L) of material per batch (i.e., reactor contents to occupy about 60% of total volume). At 20 gal (76 L), this reactor is approximately 40 times the size of the 2-L reactor, and about 40 times less than a full-scale, 400-gal reactor. At this size, the pilot plant is portable (total system weight is approximately 160 kg). Furthermore, the pilot system uses industrial components and can provide operability data that are applicable to a full-scale treatment system. Finally, at 12 gal per batch, the quantity of reagents and waste generated from testing is manageable in terms of cost, time, and logistics.

Heat is supplied to the reactor with four 2-piece mica band heaters. Each band is rated at 2250 W at 208 VAC (1-phase). The bands are controlled with a Watlow SCR power controller and a Watlow temperature controller. The temperature controller is operated with a thermocouple located inside the reactor.

For a 12-gal batch (approximately 46 kg), with an average heat capacity of 2.8 W/m^2-°C, heating the contents of the reactor from 25°C to 350°C requires an energy input of 9 kWh. Heating the stainless steel reactor itself, which weighs approximately 100 kg, requires an additional 4.5 kWh. Therefore, with a total output of 9 kW (i.e., 4 x 2250 W), it is theoretically possible to heat the reactor and contents from 25°C to 350°C in about 90 min. The heating rate that would be pursued in a run would be much lower than this to prevent potential instabilities (i.e., boilovers and foaming events).

Table 5.1. Major Components of the 20-gal Stirred-Tank Reactor System

Item No.	Item Name	Item Description
T100	Stirred-tank Reactor	18 in. diam. x 22 in. H x 3/16 in. wall, 304L SS; 0.5 in. 304L SS bottom; carbon steel lid
HR100	STR Heaters	4 Watlow two-piece mica band heaters 2250 W, 208 VAC, 1-ph Part No. B18A02 AP-727
HR101	Temp. Control Panel	14.4 kW, 240 VAC 1-ph, includes: Watlow Temp. Controller Model 988B-11FD-JRRR, Watlow DIN-a-Mite Power Controller Model DC1V6524-F0S2.
MI100	Reactor Mixer	1/2 hp TEFC 1150 rpm motor, 230 VAC, 1-ph; gear reducer to provide 230 rpm output, low-pressure chemical-type stuffing box shaft seal, 5/8 in. diam. shaft with 6 in. diam. propeller, 304 SS (MixMor Model FGL-14)
HX100	Condenser	Spiral plate heat exchanger, 3.78 ft^2 heat transfer area, water as cooling medium, 316-L SS (Spirec Model K-1)
T101	Condensate Receiver	3 gal; acrylic tank (8 in. OD x 21 in. H)
CF100	Carbon Filter	2 3/4 in. diam. x 10 in. granular activated carbon filter
V100	Pressure Relief Valve	1 in. x 1 1/2 in. pressure relief valve set at 5 psig, bronze with viton resilient, C/N packed lever (Kunkle Model 918BFEV03)

A spiral plate heat exchanger with 3.78 ft^2 of heat transfer area was selected for the condenser (Spirec Model K-1) to cool the offgas and condense organic and water vapors. Based on vendor literature, the heat exchanger should be capable of condensing up to 1 kg of steam per minute, which is well above the projected instantaneous steam generation rate in a worst-case boiling event, based on experience in Guam with the 400-gal reactor and the 2-L STR.

For the pilot-scale system, the condenser was installed in a downflow configuration. Condensed steam and oil flow into the condensate receiver and do not reflux back into the reactor. The strategy behind this configuration is to enhance safety by minimizing the amount of condensed steam that potentially may drop back into the reactor and cause vigorous boiling or steam deflagrations. A disadvantage of operating the condenser in a downflow mode is that condensed organic vapors are not refluxed and returned to the reactor, and the potential exists to collect a larger quantity of organic condensate. The exit gas from the condensate receiver tank is polished in a GAC filter before it is vented.

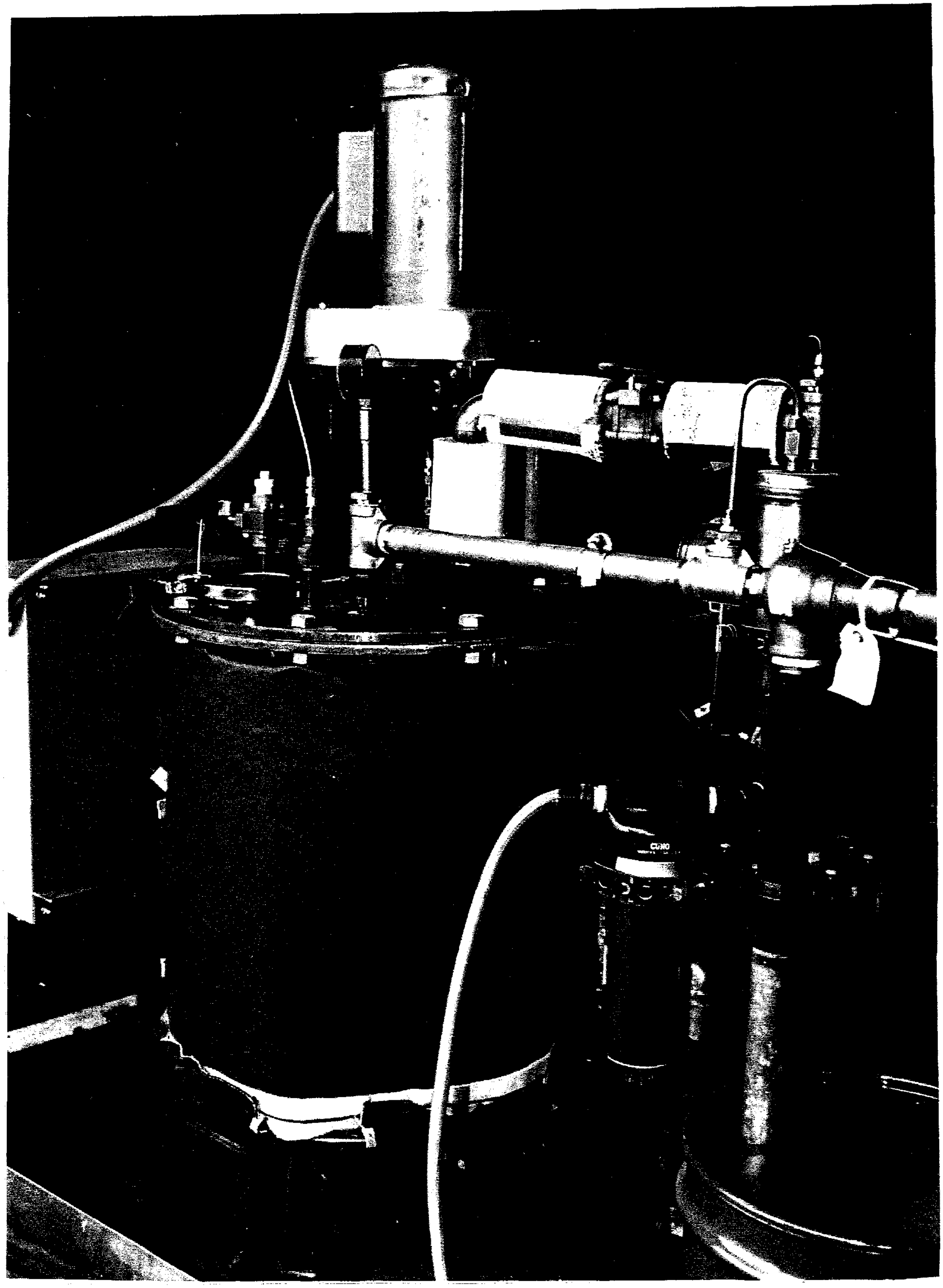


Figure 5.1. 20-gal Stirred-Tank Reactor System

The reactor is purged with nitrogen during the reaction to eliminate the possibility of exceeding flammability limits in the vapor space of the STR. The oxygen concentration in the offgas is monitored periodically with an O_2 monitor.

Agitation is provided with a gear-driven, flange-mounted, propeller-type mixer. The propeller was sized at 1/3 the tank diameter. Integrally fabricated into the flange is a standard, low-pressure, chemical-type stuffing box with two rings of packing. The maximum pressure rating of the stuffing box is 10 psig. With the gear reduction, the final output speed to the propeller is approximately 230 rpm. The gear reduction provides high torque for mixing high-viscosity, high-solids-containing slurries. Additionally, by lowering the propeller speed with gear reduction, the potential for foaming decreases.

The STR is also equipped with a 1 in. x 1 1/2 in. pressure relief valve set at 5 psig. The vent line is submerged in a steel drum filled with approximately 10 L of oil to quench and scrub any material that would be released.

A piping and instrumentation diagram (P&ID) for the STR is shown in Figure 5.2 to illustrate the relative placement of the various components on the STR system. Two thermocouples located in the reactor measure the reactor slurry temperature and should be within several degrees of each other. There is also a thermocouple in the reactor headspace or plenum (referred to as plenum thermocouple). Temperature across the condenser is also monitored. A (0 - 110 mm Hg) magnahelic pressure gauge has been installed to measure headspace pressure.

5.2 Operating Strategies

The current operational setup is similar to the liquid-phase BCD reactors being used at BCL and by other experienced groups. Additionally, four tests with the 400-gal STR were conducted with PCB in Guam (November 1994 through May 1995), and, as discussed in Section 4.0, a number of 2-L STR runs with PCB-containing feed have been conducted at PNNL. The operating strategies outlined below have been successfully demonstrated.

The feed for the liquid-phase testing consists of a bulk medium, BCD reagents, and the target contaminated constituent(s). The bulk medium, consisting of either LW-104, LW-110, Fuel Oil #6, or a similar medium, is placed into the reactor. The reagents and PCB-contaminated constituents are added to the reactor volume. The final volume of material inside the reactor, for the initial runs, is approximately 60% of the total reactor volume. The offgas system includes a water-cooled heat exchanger/condenser, a condensate receiver tank, and a GAC bed. The system also incorporates the use of a pressure relief system that vents to a knockout vessel. During the experiment, the purge gas (N_2 or other inert gases) is continuous and as low as possible. The heat cycle is initiated and the reactor is held at temperature for the allotted time, during which samples may be taken. Cooldown is accomplished by turning off the heaters and engaging the external cooling coils. The insulation blanket on the top of the reactor may be removed to facilitate faster cooldown.

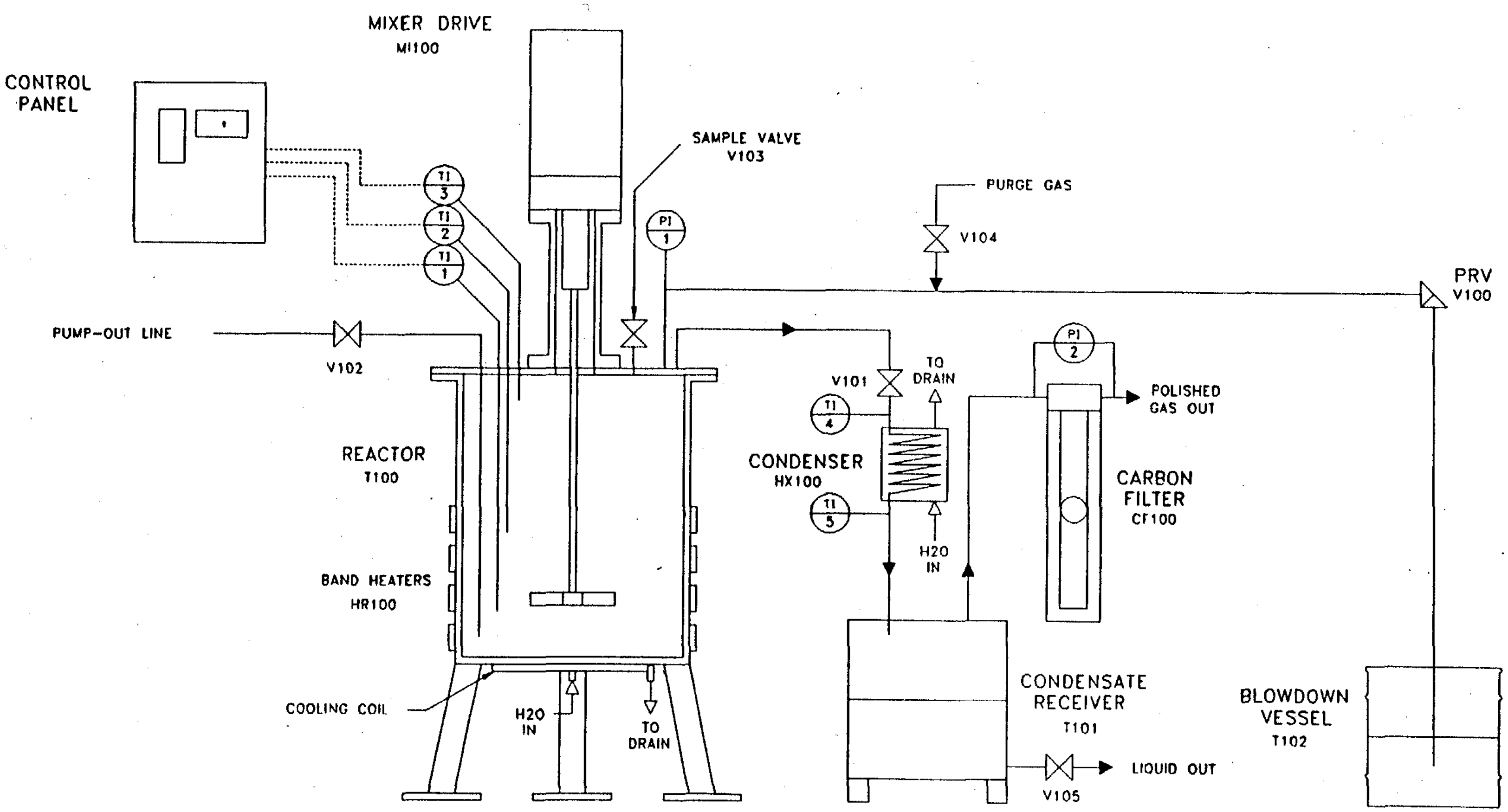


Figure 5.2. Piping and Instrument Diagram for 20-gal STR System

The feed constituents available for testing range from soft solids to hard brittle solids in a wide variety of sizes. Size reduction operations were performed on some feeds to reduce the sizes to less than 7 x 14 cm to facilitate reactor loading.

Because the 20-gal STR system is operated at temperatures near or above the auto-ignition temperatures of some of the constituents in the reactor, precautions have been taken to exclude the presence of air (oxygen) from contact with the heated reactor contents. As demonstrated during STR operations in Guam (May 1995), as the reactor heats up to the target temperature range of 340°C to 370°C, volatile organics are formed from the high-boiling-point oils (via cracking reactions). These volatile organics, along with steam and low-molecular-weight oils, purge the reactor head space and offgas lines (i.e., oxygen is displaced); consequently, the probability of ignition is small. However, as a precautionary measure, a nitrogen purge was added to the system as further protection against inleakage of air. During operations above 250°C, the nitrogen purge was turned on. Nitrogen flow was verified via observing the rotameter.

Experience with the 2-L STR has shown that with the wool felt and paint chips feedstocks most water is removed from the reactor at temperatures between 160°C and 230°C. Rapid boiling can occur that has the potential to create pressure fluctuations (4 - 40 mm Hg). During rapid boiling, it is also possible to strip organics from the reactor matrix. Consequently, it is desirable to remove water in a quiescent manner. Based on extrapolation of bench-scale data, the water removal rate from the 20-gal STR was maintained at or below 60 mL/min with wool felt and paint chips as the waste matrices. Upon initiation of water removal, the reactor temperature was walked up while keeping the water removal rate below 60 mL/min. As operating experience was gained, this target rate was increased or decreased as appropriate. Once water was removed (reactor temperature of 230°C—based on testing with the 2-L STR), the reactor could be rapidly heated to the target operating temperature. Based on success with recycling condensate during the 2-L bench-scale runs, the condensate was recovered and used for feed in subsequent runs. The purpose of this strategy was to minimize waste condensate and lower the cost of reagents.

5.3 Run Summaries

5.3.1 Shakedown Runs

Once the pilot STR reactor was assembled and the operability of the individual components verified, shakedown testing of the integrated system was initiated (June 12, 1996). For the initial test, approximately 60 kg of water were added to the reactor. The water was quickly heated to 100°C, and the contents began to boil. The power to the reactor heater was engaged at 100% output to determine the maximum effective energy input and to evaluate the performance of the condenser. Condensate was collected and measured, and it was determined that the system was capable of boiling approximately 12 kg/hr of water, i.e., effective energy delivery of 7.5 kW. Based on the rating of the heaters

(9.0 kW at 208 v), approximately 17% of the energy input into the heaters was lost. With an effective delivery of 7.5 kW, the reactor and contents can be heated at a rate of about 4°C/min. For comparison, this is about a factor of 7 greater than the maximum heating rate achieved with the 400-gal STR in Guam.

This test also showed that the reactor condenser (3.7 ft^2 of heat transfer area) was capable of condensing the steam and cooling it to approximately 40°C using cooling water at approximately 25°C. This test also showed that the condenser could handle the maximum energy input from the reactor, and offgas temperature excursions downstream of the condenser should not occur. The ability to quench the temperature of the reactor offgas is important to minimize emissions, and to protect operators and equipment from high temperatures.

After successful testing with water, the reactor was loaded with 37.5 kg (44 L) of clean oil for further shakedown testing. A small quantity of water remained in the reactor. Bumping and popping could be heard as water was boiled out of the oil at temperatures from 175°C to 325°C. It is speculated that the water was still being removed at very high temperatures partially because no heaters were located around the outside of the reactor head space. Since the head of the reactor was cooler, water vapor may have condensed on the inside top of the reactor and dropped back into the oil. The presence of the water did not cause any operational difficulties; however, the pressure inside the reactor oscillated between 6 and 15 mm Hg while water was being boiled out of the oil.

During the testing with oil, the reactor contents were easily heated to 360°C. The reactor was purged with nitrogen gas to eliminate the potential for ignition.

5.3.2 PR1 (6/19/96) - Pilot-scale Reactor Run 1

5.3.2.1 Objectives/Conditions

The objective of PR1 was to operate the pilot-scale system using information and run conditions from bench-scale system runs R14 and R16 with wool felt as a feedstock and addition of the BCD recipe with the Battelle reagent. The BCD Group reagent to prevent product solidification was also added to the reactor contents.

The reactor was loaded with 9.39 kg wool felt that was determined to contain 32% PCB by weight (total of 3.0 kg PCB). Base was added at a ratio of NaOH equivalents:PCB of 1.8:1, or 72% of the baseline addition ratio of 2.5:1. Oil (LW-104) was added at a ratio of 3:1 (oil:wool felt). The BCD Group reagent was added at a ratio 2:5 (reagent:NaOH).

For this run, the reactor was heated to 275°C and held there for 4 hr. Samples were pulled at 90°C; 230°C; and at 0, 1, 2, and 4 hr while at 275°C. A material balance for Run PR1 is given in Table 5.2. Before this run, it was believed that the wool felt feedstock was equivalent to that used in the bench-scale runs. For the bench-scale runs, the wool felt was found to contain approximately 14%

Table 5.2. Material Balance for PR1

Stream	Total Mass/Volume	PCB Concentration, ppm[a]
Feed	46 kg	73,000
Wool Felt	9.4 kg	320,000
NaOH	2.8 kg	0
Battelle Reagent	4.5 kg	0
BCD Group Reagent	1.1 kg	0
LW-104	28.2 kg (8.7 gal)	0
Reactor Contents		
at 230°C, 0 hr	~45 kg	48,000
at 275°C, 0 hr	~42 kg	28,000
at 275°C, 1 hr	~41 kg	16,000
at 275°C, 2 hr	~41 kg	14,000
at 275°C, 4 hr	~41 kg	7,200
Aqueous Condensate	1.9 kg	< 100
Organic Condensate	3.0 kg	730

(a) Reported PCB concentration has not been corrected for interference, contamination, or baseline noise.

PCB by weight. While it was thought that the NaOH equivalents to PCB ratio was 4.25:1, it was actually 1.8:1. As a result of this underloading, the treatment target (i.e., less than 2 ppm per PCB congener) was not achieved after 4 hr at temperature. However, greater than 90% reduction of PCB was achieved as the concentration was reduced from approximately 73,000 to 7200 ppm.

5.3.2.2 Run Observations and Findings

The reactor contents were heated from 22°C to 120°C in about 20 min. However, a 50°C temperature discrepancy existed between the two thermocouples in the oil slurry. This discrepancy was likely caused by agglomerated wool felt sticking to one of the thermocouples and effectively insulating it from the hotter oil. After reaching a reactor temperature of 190°C, both thermocouples read within several degrees of each other. At a temperature of approximately 180°C, boiling of water inside the reactor was audible; however, no condensate was collected until a reactor temperature of 190°C was reached.

After it reached 190°C, the reactor was heated up to 230°C in about 20 min. Within 10 min of the set point change, the reactor had reached 200°C, and the indicated pressure in the reactor rapidly increased from 4 mm Hg to 13 mm Hg. The rapid heating in this temperature range provided an opportunity to examine how the system performed under potentially unstable boiling conditions.

When 230°C was reached, it was observed that the temperature of the offgas at the condenser inlet had increased from 75°C to 171°C, while the plenum temperature in the reactor had increased from 81°C to only 110°C (i.e., the offgas going into the condenser was showing a higher temperature than the offgas inside the reactor). Based on previous experience in Guam and with the bench-scale testing, such a cross-over in temperatures can generally be attributed to boilover or foaming of the reactor contents. However, later it was determined that the temperature cross-over was most likely due to the placement of the reactor plenum thermocouple in a space partially shielded and insulated from the open head space area (observed during a post-run inspection).

When the temperature of the reactor reached 200°C, the odor of ammonia was detected in the offgas vent line downstream of the carbon bed. Also at this time, it was observed that more gas was exiting the vent line than was being added to the system in the nitrogen purge. A wet test meter was placed on the offgas line to record gas generation rates during the remainder of the test. Measured gas flow rates (minus the flow rate of the nitrogen purge) during the high condensate collection period were as high as 4 L/min, and slowly decreased to 0.7 L/min while the reactor was held at 230°C for about 30 min. While at the hold temperature of 275°C, offgas flow rates averaged approximately 0.25 L/min. During testing with the 400-gal STR in Guam, nominal offgas flow rates downstream of the condenser were on the order of 0.25 L/min for the entire runs.

Operations during the 4 hr at the hold temperature (275°C) were uneventful. To maintain temperature, the power output to the heaters was about 9%. The reactor was sampled two times in this period before final shutdown.

Condensate generation during the pilot-scale run was similar to that predicted from similar bench-scale runs. Figure 5.3 shows the condensate generation profile during the course of the run. Table 5.3 compares the condensate generation data from the bench-scale run R14 with the first pilot-scale run, PR1. Aqueous condensate generation numbers were essentially equivalent; however, a much greater fraction of the reactor contents came off during the pilot run as organic condensate. This increase is partially attributed to the more aggressive heating strategy pursued while heating the reactor between 190°C and 230°C. For R14, the reactor was heated from 190°C to 230°C in about 45 min as compared with 18 min for the pilot run. In increasing from 230°C to the target temperature of 275°C, 1 hr was taken for the pilot run as opposed to 30 min for the bench-scale run.

The unusually high rates of organic condensate collection is presumably due in part to the downflow condenser that was used on the reactor. Condensed oil flows into the condensate receiver and does not reflux back into the reactor.

5.3.2.3 Cleanout and Disassembly

Run shutdown and cooldown consisted of engaging the cooling coils attached to the bottom of the reactor and removing the top and side insulation from the vessel. Cooling was promoted through use of a large fan that was used to blow air across the top of the reactor and an air line used to blow air across the sides of the reactor. The forced-air cooling mechanisms were not in place during the first

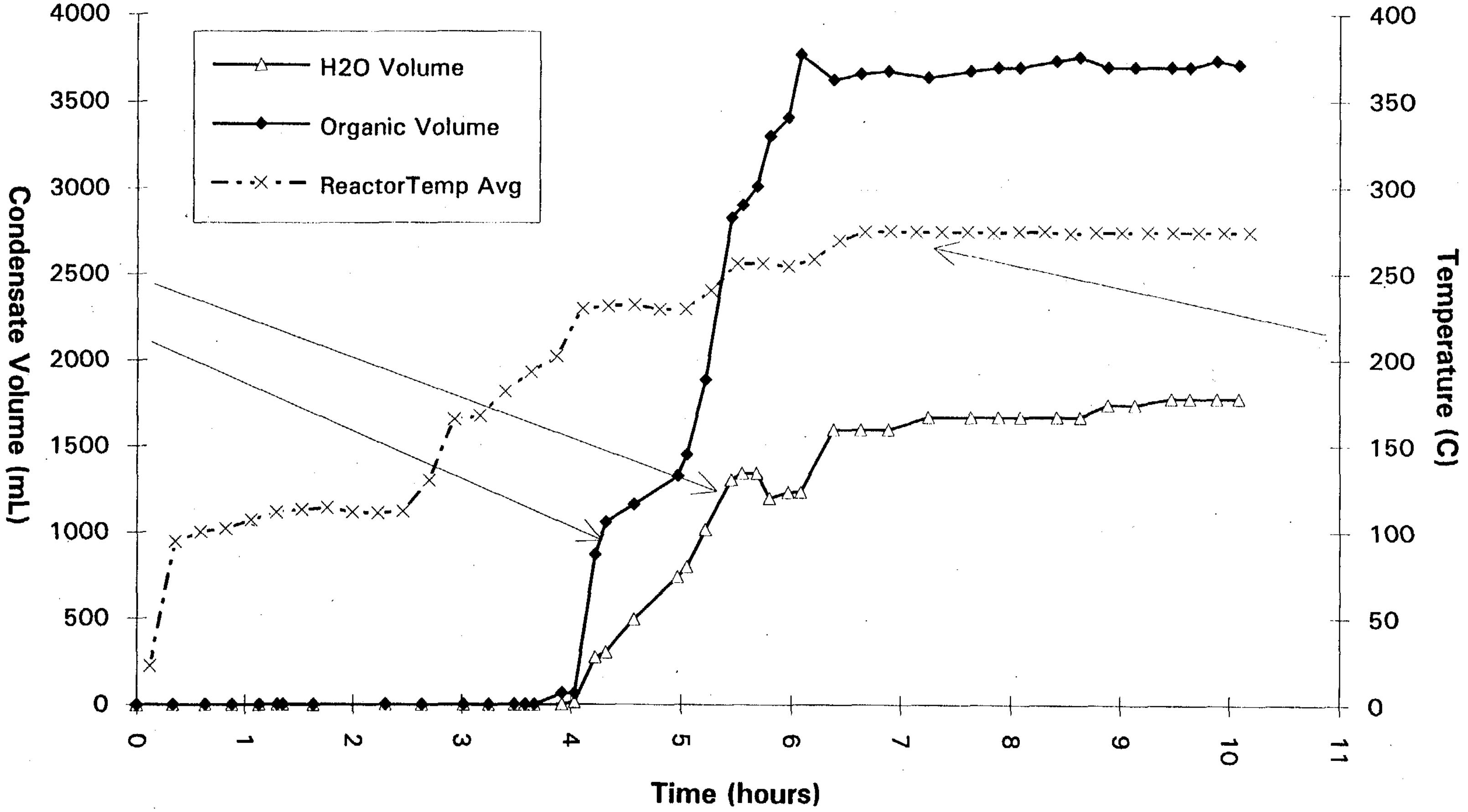


Figure 5.3. Temperature and Condensate Generation Profile for PR1

Table 5.3. Bench-scale and Pilot-scale Condensate Generation Comparison

	Bench Run R14	**Pilot Run PR1**
Total Feed Mass, kg	1.29	46
Oil:Wool Felt, Mass Ratio	3:1	3:1
Wool Felt:Total Base, Mass Ratio	1.3:1	1.3:1
BCD Group Reagent:NaOH	0%	40%
Total Aqueous Condensate, g (% of total feed mass)	53.1 (4.1%)	1940 (4.2%)
Total Organic Condensate Generated, mL (% of total feed mass)	47 (3.1%)	3350 (6.3%)
Condensate Generated at 275°C During 4 hr Hold Time:Aqueous, g/organic, mL	1/5	540/0
Total Condensate as wt% Feed	7.2%	10.5%

20°C degree drop, but, overall, the reactor dropped from 275°C to 245°C in 30 min and from 245°C to 191°C in 28 min. At this point, the reactor was prepared for discharge. For discharge, the reactor was sealed off and pressurized to between 40 mm Hg and 150 mm Hg. The valve was opened on the discharge line which connects to a dip leg in the reactor, and the product began flowing into a metal container at a rate of 0.5 to 1 gpm. The flow tended to be intermittent, and the reactor had to be pressurized several times.

A heel of solids was observed when the loading port on the reactor was opened. The 5-cm-deep heel was composed of black, granular, oil-coated solids, similar to what had been recovered in bench-scale runs. The solids level was about 1 to 3 cm below the agitator and was evenly distributed across the reactor bottom, with one exception. Around the dip leg, solids were carried away by the escaping liquid during discharge, creating a 10- to 15-cm-diameter crater. The crater was still visible 15 hr after the reactor was turned off, indicating that the heel of solids was dry and nonflowable. The agitator shaft was coated with between 1 and 3 cm of solids, the heaviest being at the top (presumably the initial liquid surface level). The thermocouples were all fairly clean and free of significant buildup. The inside walls of the reactor were also fairly clean, with a small amount of extra buildup at the level of the residual solids in the bottom. After the material balance was completed, approximately 9 kg of material were estimated to remain in the reactor (i.e., about 20% of the initial feed mass). The treated product, in metal containers, was allowed to settle, and approximately 70% of the oil (including the organic condensate) initially charged to the reactor was recovered for reuse in the next run.

5.3.3 PR2 (6/25/96) - Pilot-scale Reactor Run 2

5.3.3.1 Objectives/Conditions

The primary objective of Run PR2 was to duplicate PR1, using the recovered organic and remaining heel from the first run. The quantity of the BCD Group reagent was reduced by 50%. Reducing the quantity of organic condensate generated was attempted by using a less aggressive heating ramp rate to bring the reactor contents up to the target temperature. When PR2 was conducted, analytical results from PR1 were not yet available.

The reactor was loaded with 9.7 kg wool felt. Base was added at a ratio of NaOH equivalents:PCB of 1.8:1, or 72% of the baseline addition ratio of 2.5:1. Recovered oil from PR1 (15.4 kg) and organic condensate (3.0 kg) and virgin LW-104 (9.8 kg) were added to give a ratio of 3:1 (oil:wool felt). The BCD Group reagent was added at a ratio 1:5 (reagent:NaOH). The residual heel of solids from PR1, approximately 5 cm deep and weighing an estimated 9 kg, remained in the reactor. It was planned to collect additional information on buildup/accumulation of solids in the reactor.

For this run, the reactor was heated to 275°C and held there for 4 hr. Samples were pulled at 90°C; 230°C; and at 0, 1, 2, and 4 hr while at 275°C. A material balance for Run PR2 is given in Table 5.4.

The reactor was heated over a 2-hr period to 170°C, at which time condensate began to be collected. At about 150°C, offgas generation increased from about 0.25 L/min to between 2 L/min and 4 L/min. Very little offgas was generated until the temperature in the reactor reached about 150°C. Figure 5.4 shows the gas generation profile as a function of time and temperature. The temperature was gradually increased from 170°C to 230°C over a 2-hr period. Heating from 230°C to the target temperature, 275°C, was done in 80 min.

Figure 5.5 shows the aqueous and organic condensate generation, along with temperature profiles, for this run. Significant organic condensate was generated after the target temperature was achieved and aqueous condensate generation had stopped. This did not occur during the bench-scale testing and was likely the result of the vessel geometry and the fact that less heat transfer per unit volume of the reactor contents was available. With less area available to transfer heat, the wall temperatures for the pilot reactor are most likely higher than those in the bench-scale system. Consequently, the LW-104 oil may be volatilized at the vessel walls. Overall, the condensate generation profiles for PR1 and PR2 are quite similar (Table 5.5). The most notable difference is that between 190°C and 230°C, more organic condensate was generated during PR1.

5.3.3.2 Cleanout and Disassembly

After completion of PR2, analytical results were obtained indicating that the PCB concentration had not been reduced to the target treatment standard. Therefore, the contents were left in the reactor for re-treatment in Run PR3.

Table 5.4. Material Balance for PR2

Stream	Total Mass/Volume	PCB Concentration, ppm[a]
Feed	55.5 kg	73,000
Wool Felt	9.6 kg	320,000
NaOH	2.8 kg	0
Battelle Reagent	4.5 kg	0
BCD Group Reagent	0.56 kg	0
Oil	28.9 (8.9 gal)	3,900
Heel	~9 kg	7,200
Reactor Contents		
at 98°C, 0 hr	~45 kg	Not Available
at 275°C, 0 hr	~42 kg	18,000
at 275°C, 1 hr	~41 kg	17,000
at 275°C, 2 hr	~41 kg	16,000
at 275°C, 4 hr	~41 kg	13,000
Aqueous Condensate	2.0 kg	1
Organic Condensate	2.4 kg	1,500

(a) Reported PCB concentration has not been corrected for interference, contamination, or baseline noise.

5.3.4 PR3 (6/27/96) - Pilot-scale Reactor Run 3

5.3.4.1 Objectives/Conditions

The objectives of PR3 were to add additional base and the Battelle reagent to the unsuccessfully treated product from PR2. Because the PCB concentration in the wool felt was twice the expected level, the quantities of NaOH and Battelle reagent were doubled from the original level at the start of PR2. Another objective of this run was to evaluate the effects of reprocessing feed (including the heel from PR1) on solids accumulation and reactor cleanout.

For this run, the reactor was heated to 275°C and held there for 4 hr. Samples were pulled at 90°C; 230°C; and at 0, 1, 2, and 4 hr while at 275°C. A material balance for Run PR3 is given in Table 5.6.

Upon completing PR2, the contents were left in the reactor, and the reactor was held at about 100°C (with agitation) for approximately 36 hr. The temperature was maintained at 100°C to prevent solids from settling. Additional NaOH and Battelle reagent were added to the reactor, and PR3 was

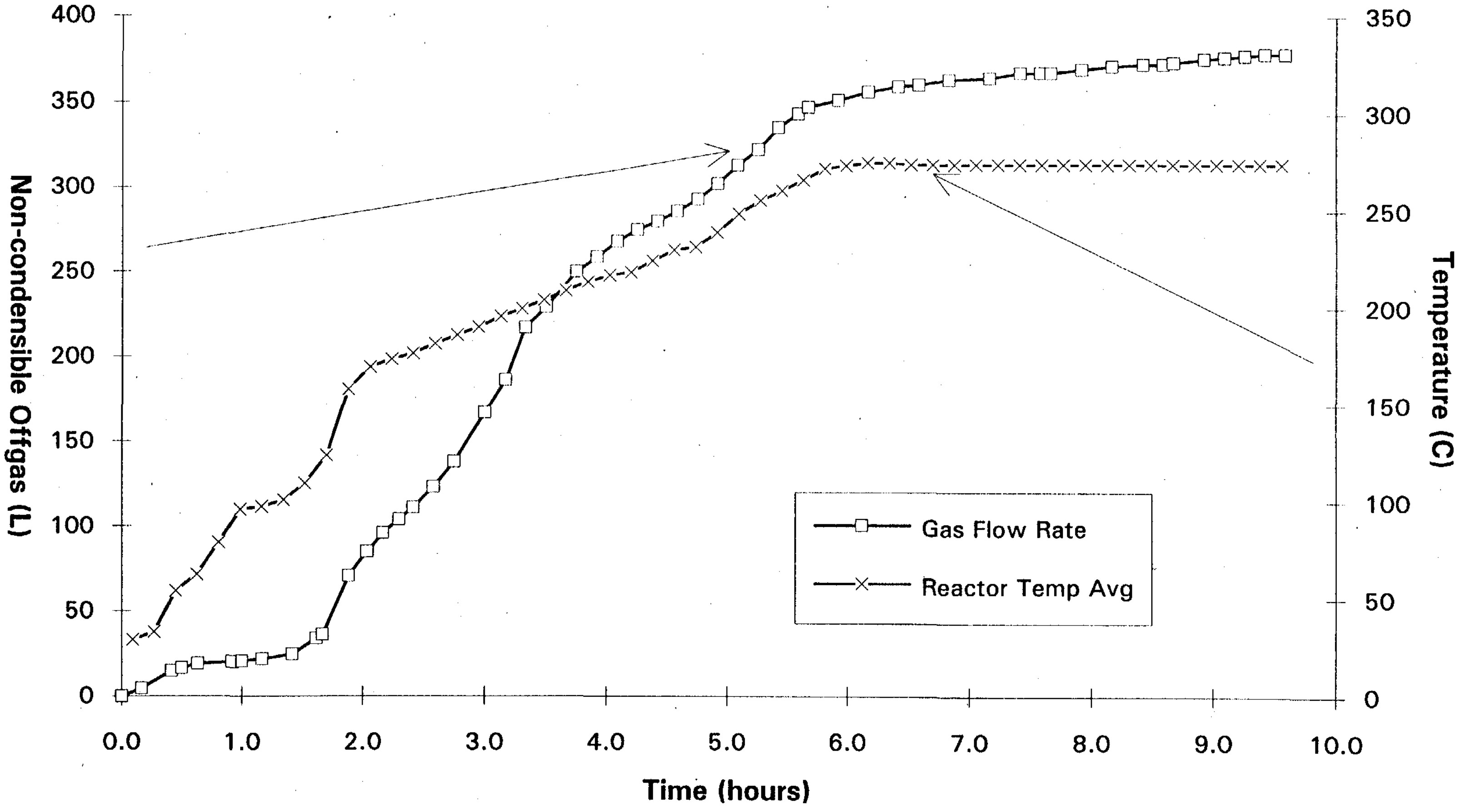


Figure 5.4. Noncondensible Offgas Generation Profile for PR2

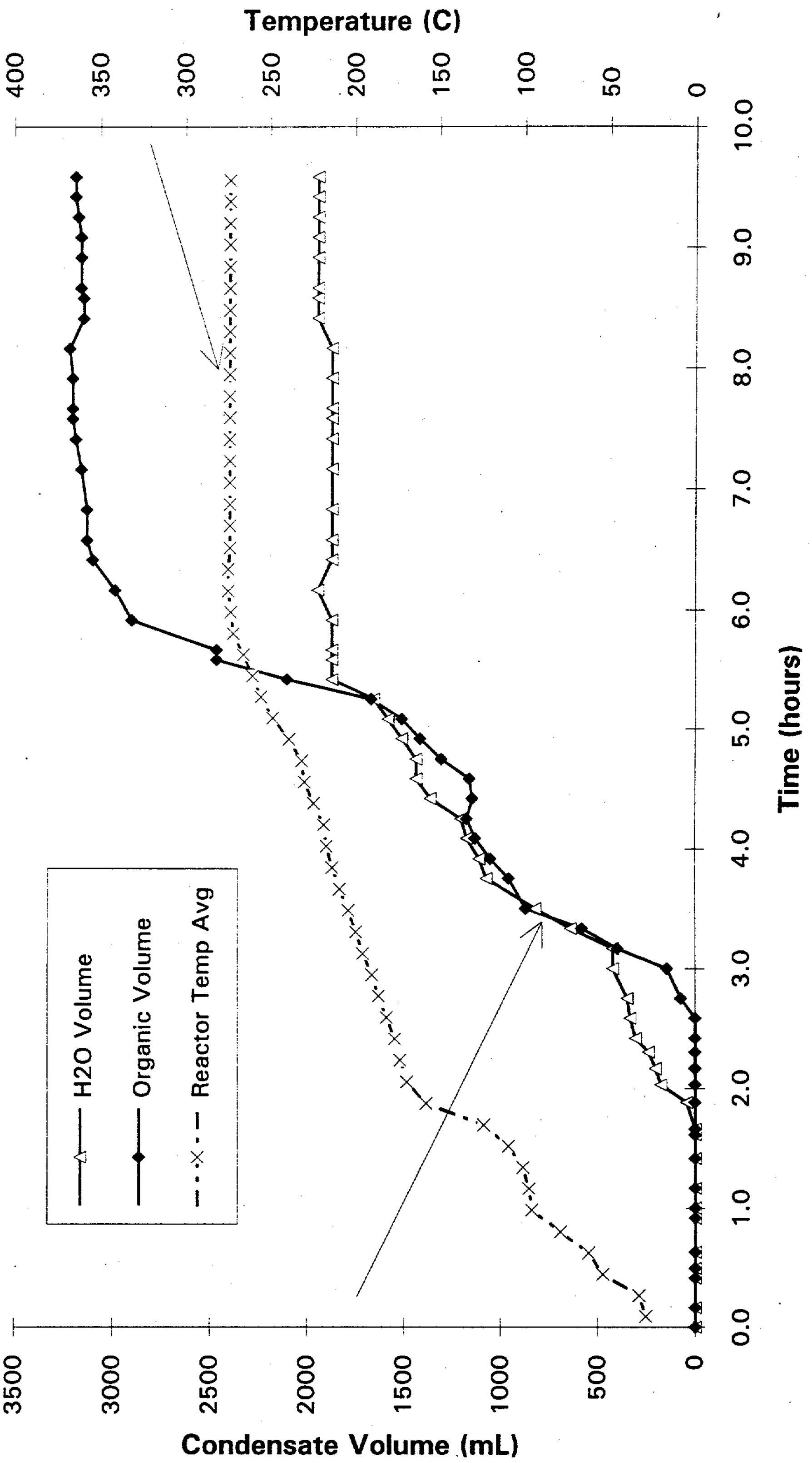


Figure 5.5. Temperature and Condensate Generation Profile for PR2

Table 5.5. Pilot-scale Condensate Generation Comparison, PR1 and PR2

	Pilot Run PR1	**Pilot Run PR2**
Total Feed Mass, kg	46	46.5 (55 kg with heel)
Oil:Wool Felt, Mass Ratio	3:1	3:1
Wool Felt:Total Base, Mass Ratio	1.3:1	1.3:1
BCD Group Reagent:NaOH	40%	20%
Total Aqueous Condensate, kg (% of total feed mass)	1.94 (4.2%)	1.96 (4.2%)
Total Organic Condensate Generated, mL (% of total feed mass)	3350 (6.3%)	2780 (5.1%)
Condensate Generated at 275°C During 4 hr Hold Time:Aqueous, g/organic, mL	540/0	73/725
Total Condensate as wt% Feed	10.5%	9.6%

initiated. Very little water was present in the slurry, so the reactor was quickly heated from 110°C to 230°C during a 2-hr period. Significant organic condensate began to be generated when the contents of the reactor were heated to 250°C. Figure 5.6 shows the condensate generation profile for Run PR3. While heating the reactor contents between 250°C and 275°C, approximately 7 L of organic condensate were collected. Heavy organic condensate continued until the reactor had been held at 275°C for about 1 hr.

Noncondensible offgas generation was fairly constant throughout the run (Figure 5.7). During PR2, the offgas generation rate tapered off shortly after achieving the target temperature.

In comparing PR3 with the previous two runs, about three times as much organic condensate was generated. Also about 30% more noncondensible offgas was generated in PR3 than during PR2. Plausible explanations for these differences are 1) additional NaOH added in PR3 acted to break down organics; 2) recycled oil and organic condensate breaks down more readily than virgin oil; and/or 3) buildup of material at the reactor wall resulted in higher wall surface temperatures required to heat and maintain the reactor at the target temperature. During the first run (PR1), to maintain the reactor at 275°C, the heaters operated at an average output of 9%, with heater surface temperatures between 304°C and 310°C. During the second run (PR2), the heater power output at 275°C was 13% to 14%, with corresponding heater surface temperatures of 316°C to 320°C. During Run PR3, the output increased to 14% to 16%, with heater surface temperature increasing to between 322°C and 329°C.

Table 5.6. Material Balance for PR3

Stream	Total Mass/Volume	PCB Concentration, ppm[(a)]
Feed	60.8 kg	
(From PR2		13,000
Wool Felt	9.6 kg	
NaOH	2.8 kg	
Battelle Reagent	4.5 kg	
BCD Group Reagent	0.56 kg	
Oil	28.9 (8.9 gal)	
Residual Heel)	~9 kg	
Additional Reagents		
NaOH	2.8	0
Battelle Reagent	4.5	0
Condensate from PR2	2.4 kg	1,500
Reactor Contents		
at 230°C, 0 hr	~60 kg	Not Available
at 275°C, 0 hr	~53 kg	830
at 275°C, 1 hr	~51 kg	18
at 275°C, 2 hr	~51 kg	11
at 275°C, 4 hr	~51 kg	7
Solids Chipped from Reactor	residual heel	6
Oil Field Blank	(measure of interference)	6
Aqueous Condensate	0.73 kg	1
Organic Condensate	7.9 kg	2,800

(a) Reported PCB concentration has not been corrected for interference, contamination, or baseline noise.

Testing with the 2-L STR, especially Run R8, showed that large quantities of LW-104 oil will volatilize at temperatures around 290°C. Consequently, it is possible that during PR3, hot spots along the reactor wall led to the higher organic condensate generation.

5.3.4.2 Cleanout and Disassembly

After the reactor was operated at 275°C for 4 hr, the power to the heaters was shut off, and the insulation blanket was removed. The external cooling coils were engaged, and air was directed at the reactor with a fan and an air line. When the contents cooled to 180°C, the reactor vent line was closed and the reactor was pressurized to 60 - 90 mm Hg to pump out the reactor through the dip leg. Of the estimated 51 kg of material in the reactor, 23 kg were removed. After cooling overnight, the reactor

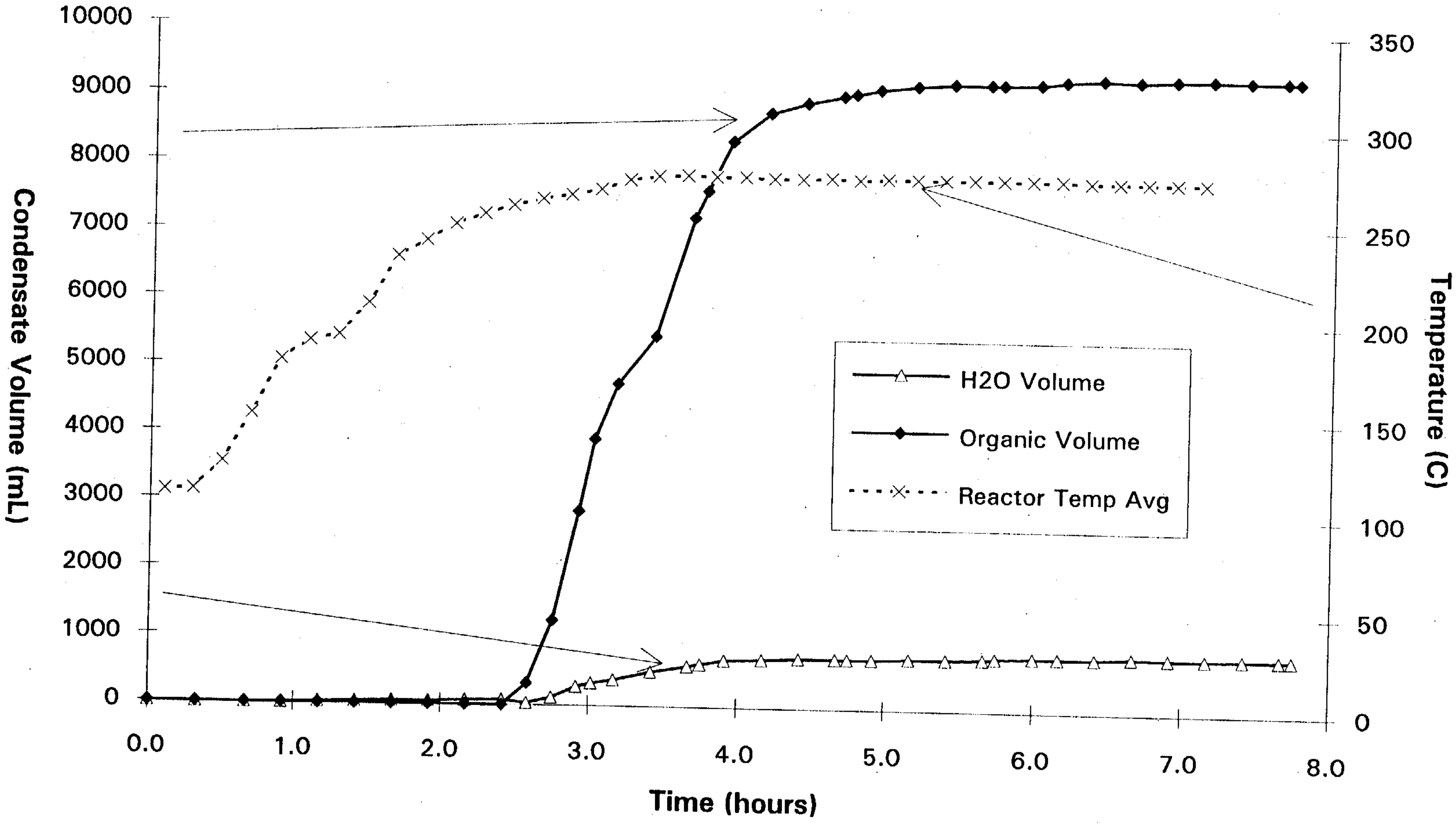


Figure 5.6. Temperature and Condensate Generation Profile for PR3

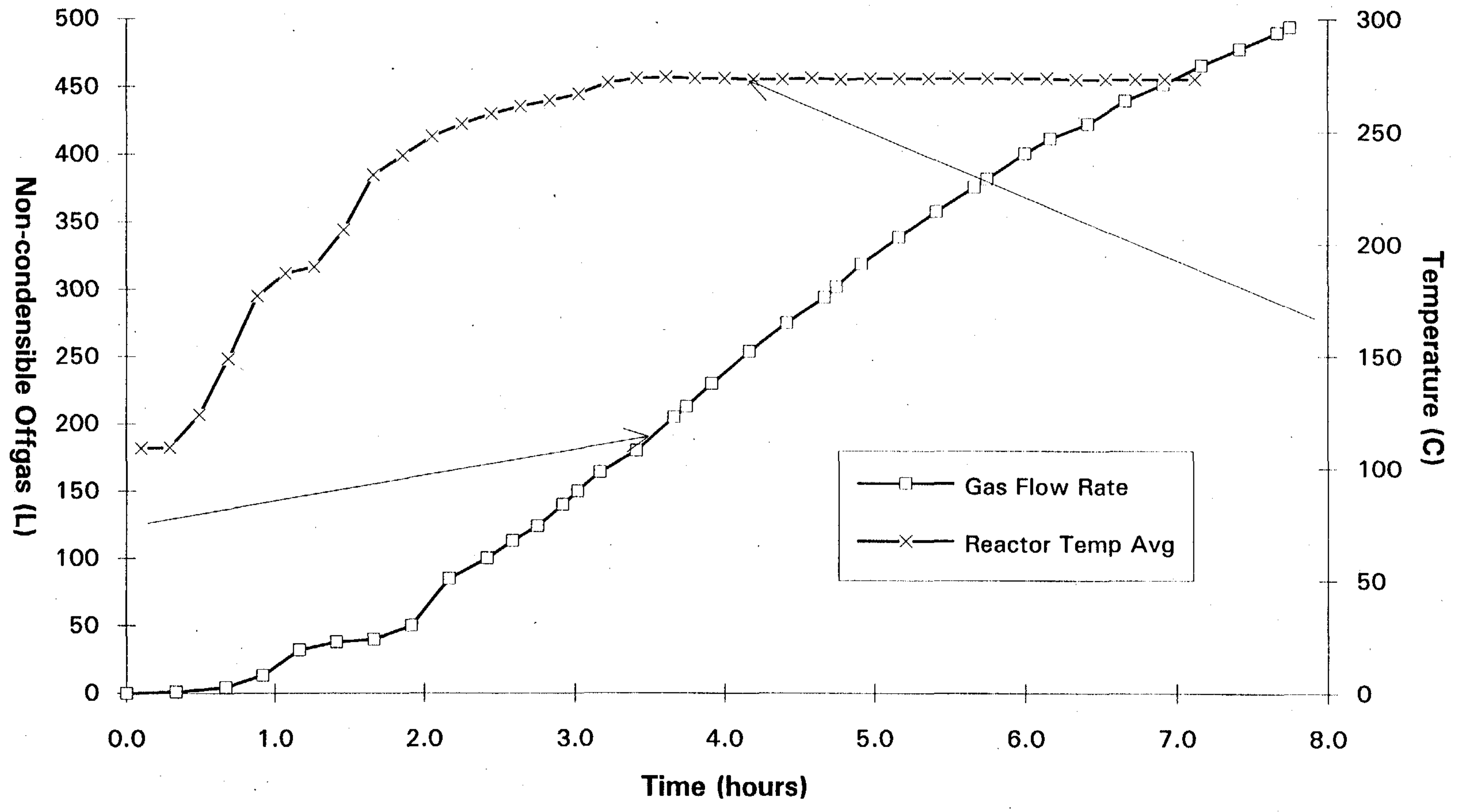


Figure 5.7. Noncondensible Offgas Generation for PR3

was opened and a large heel of sludge was observed. A sludge layer 5 to 10 cm thick lined the walls and bottom of the reactor. The material was fairly soft and could be scraped off the reactor walls with a metal rod.

The geometry of the distribution of the sludge indicated that material accumulated preferentially where cooling air had impinged on the outside of the reactor and above the cooling coils on the tank bottom. This area was also outside the direct influence of the agitator. The space around the dip leg was free of accumulation. It was speculated that the manner in which the reactor was cooled caused solid material to freeze. To test this hypothesis, approximately 1 L of oil was decanted from the material pumped out of the reactor the previous day and was added back to the reactor. A rod was used to knock down material adhering to the sides of the vessel, and the system was reheated to approximately 180°C. The reactor was sealed and pressurized to pump out additional material. This approach was used to pump out an additional 13 kg of material for a total removal of 36 kg. The sludge removed was allowed to settle for several days and was then decanted. From the 36 kg of sludge, 3.4 kg of oil were recovered. The recovered oil was added back into the reactor, and it was heated to 200°C and pumped out. This time, 8.8 kg of material were recovered, with 4.92 kg of oil and 3.88 kg of additional solids. Thus, a total of 41.4 kg of material were recovered prior to reactor disassembly and cleanout.

Including the organic condensate, 12.8 kg of organic oil were recovered from this run for potential reuse in subsequent runs. This amount represents only 44% of the oil initially added to PR2 and PR3. After PR1, approximately 70% of the organic oil was recovered.

Reactor cleanout was facilitated by disassembling the system and removing the reactor head. During cleanout, a total of 11.8 kg of solids were removed. The distribution of solids in the reactor is shown in Figure 5.8. Most of the solids remaining in the reactor were loosely attached to the reactor walls and bottom. However, a tenaciously attached layer (1 to 2 kg) required the use of a hammer and chisel for removal. After complete removal of solids, the inside of the reactor was washed and examined for evidence of corrosion. No signs of cracks or pits were found.

5.3.5 PR4 (8/27/96) - Pilot-scale Reactor Run 4

5.3.5.1 Objectives/Conditions

The objectives of PR4 were to treat a 50/50 mixture of wool felt and paint chips using the Battelle reagent. Based on accumulation of solids on the bottom of the reactor after PR3, the oil:wool felt ratio was increased from 3:1 to 4:1 for PR4. Additionally, from observation of the treated products from the bench-scale testing with paint chips, it was thought that paint chips would likely increase the viscosity of reaction medium, which could potentially assist in keeping solids in the matrix suspended. After observing the large quantity of organic condensate generated during PR3, it was decided to use LW-110 as the reaction medium rather than LW-104. LW-110 exhibits a much higher boiling point than does LW-104. Base loading was determined by assuming the wool felt contained 35% PCB, and that the paint chips contained 1000 ppm. The estimated mass of PCB contained in the paint chips was

Figure 5.8. Distribution of Solids Remaining in 20-gal STR After PR3

multiplied by 100 (to account for NaOH consumption by the paint chip matrix). The "effective" mass of PCB in the paint chips was added to the estimated PCB mass from the wool felt. This mass was multiply by the 2.5 factor (i.e., NaOH:PCB = 2.5:1), and then divided by 2 to provide a base loading equivalent to that used for the successful pilot-scale run, PR3.

For this run, the reactor was heated to 275°C and held there for 2 hr. Next, the temperature was increased to 300°C, held for 1 hr, then bumped to 325°C and held for 1 hr. Samples were pulled at 155°C; at 0, 1, 2 hr while at 275°C; after 1 hr at 300°C; and after 1 hr at 325°C. A material balance for PR4 is given in Table 5.7.

Operations during PR4 were without event. The entire run was completed in about 7 hr. The only complication was failure of the wet test meter shortly after the run was initiated. Consequently, no instantaneous or cumulative gas flow rate information was collected during PR4. Very little condensate was collected during the run. A total of 1100 g of aqueous condensate and approximately 570 mL of organic condensate were generated. On a mass basis, the total condensate represents 4.2% of the feed mass for PR4. In comparison, the total condensate represented 10.5%, 9.6% and 14.2% for Runs PR1, PR2 and PR3, respectively. Much of this difference can be attributed to the use of LW-110 as the reaction medium for PR4. In all of the other runs, LW-104 was used. Also, it was noted previously that in PR3, maintaining the reactor at 275°C required operating the heaters at an output of 14% to 16%. For PR4, an output of 12% to 13% was sufficient to maintain the reactor contents at

Table 5.7. Material Balance for PR4

Stream	Total Mass/Volume	PCB Concentration, ppm[(a)]
Feed	38.3 kg	20,000
Wool Felt	5.1 kg	150,000
Paint Chips	5.1 kg	300
NaOH	2.9 kg	0
Battelle Reagent	4.7 kg	0
BCD Group Reagent	0.0 kg	0
Oil (LW-110)	20.5 kg (8.9 gal)	0
Reactor Contents		
at 155°C, 0 hr	38 kg	Not Available
at 275°C, 0 hr	38 kg	680
at 275°C, 1 hr	37 kg	640
at 275°C, 2 hr	37 kg	Not Available
at 300°C, 1 hr	37 kg	103
at 325°C, 1 hr	37 kg	9
Solids Chipped from Reactor	Residual Heal	10
GAC from Offgas Polishing	0.33 kg	2.3
Aqueous Condensate	1.1 kg	Not Available
Organic Condensate	0.49 kg	~6,500

(a) Reported PCB concentration has not been corrected for interference, contamination, or baseline noise.

275°C. The lower heater output required for PR4 was probably due to the extensive cleaning to remove solids accumulation along the reactor wall following PR3.

While heating the reactor from 150°C to 275°C, it was noted that the offgas contained significant ammonia, presumably from degradation of wool felt. The ammonia smell was also noted during the other 20-gal STR runs; however, the odor was much stronger during PR4. After passing through the carbon bed, the offgas was bubbled through approximately 5 cm of water to provide additional scrubbing and to maintain a slight positive pressure on the reactor. This scrubber water was allowed to evaporate, and the residuals were extracted and analyzed. No detectable PCB was found. As in some of the previous runs, offgas samples were collected and analyzed on a gas chromatograph. A sample taken during a period of rapid noncondensible offgas generation (shortly after the target temperature, 275°C was achieved) showed that the offgas was 90% hydrogen and about 6% methane. No purge gas was being injected into the STR before or during the collection of this offgas sample. A similar offgas composition was seen during PR3.

After PR4, the GAC cartridge used for offgas polishing for all four pilot-scale runs was disassembled, and the GAC was mixed and sampled. The analytical results showed that the GAC contained a total of 2.3 ppm PCB, indicating that very little PCB migrated downstream of the condensate receiver tank. At 2.3 ppm, the entire GAC bed (330 g) contained just 0.76 mg total PCB.

Examination of the analytical results from PR4 show that PCB destruction required higher temperatures than PR3, even though reagent loadings were similar. Even after 1 hr at 325°C, the treated material only marginally achieved the <2 ppm per congener treatment criterion. The difficulty associated with PCB destruction during PR4 may be partially attributed to the introduction of the paint chips. As indicated from the bench-scale test results with paint chips (Section 4.7.2), destruction of PCB in the paint chip matrix is difficult even though the PCB concentration is low. For the bench-scale testing, the paint chips feedstock contained essentially 100% paint chips. However, the paint chips feedstock for PR4 contained debris, including spent shot blast. It is possible that the debris consumed or tied up large quantities of the NaOH.

5.3.5.2 Cleanout and Disassembly

Upon completion of the run, the reactor was allowed to cool to 210°C while agitating. At this temperature, the reactor was sealed, pressurized to 75 - 110 mm Hg and pumped out via the dip leg in the reactor. The reactor contents removed via the dip leg contained almost no solids. However, after an oil material balance was performed, it was determined that about 96% of the oil added to the reactor was recovered (including approximately 0.5 kg of organic condensate) for potential reuse in subsequent runs. The high oil recovery was likely a result of using LW-110 for the run rather than the LW-104, which was used in the three previous pilot-scale runs.

Despite the higher oil:wool felt ratio, solids accumulation in the reactor was a problem. After complete cooling, the reactor head was removed and cleanout efforts were initiated. The solids in the bottom of the reactor were harder and more rock-like in character than the solids removed after PR3. Removal of the solids required the use of a hammer and chisel and about 4 hr to complete. A total of about 15 kg of hardened solids were removed. For PR4, the BCD Group reagent was not added. Additionally, the paint chips used for the run contained about 50% spent steel blasting media, which may have contributed to the formation of the hard salt cake.

6.0 Economic Assessment

The economics of the liquid-phase BCD process were evaluated in terms of capital and operating costs for a 300-gal batch system operating at a throughput of 180 kg (400 lb) per batch of wool felt and paint chips/debris. See Appendix B for the basis for the materials and operating parameters for the scaled-up system.

The following assumptions have been made:

1. System will treat one batch per day
2. PCB concentration in the wool felt is 350,000 ppm and in the paint chips is 500 ppm.
3. The system will run 5 days per week, 50 weeks per year.
4. Capital costs are depreciated over 10 years to obtain a total annual operating cost and the unit cost ($/kg) for the treated wool felt and paint chips.

6.1 Capital Costs

Equipment costs for this evaluation were based on actual equipment costs for the STR system procured for the Guam BCD demonstration conducted in 1994/1995 and from vendor quotes. These costs were escalated to May 1996 dollars. From Table 6.1, the total purchased cost for the major components in the BCD STR system were $61K at the time of purchase. In May 1996 dollars, using the Chemical Engineering Plant Cost Index (*Chemical Engineering* 1996), the total equipment cost is $110K. The 1996 equipment costs include a packaged closed-loop oil cooling system for the STR. This was not included in the actual purchased cost of the BCD system demonstrated in Guam.

In addition to the purchased equipment costs, the fixed capital investment (FCI) includes other direct and indirect costs, as shown in Table 6.2. The direct costs include installation, instrumentation and controls, piping, electrical, site preparation, and service/support facilities. Indirect costs include engineering and construction.

The ratios for the cost elements comprising the total FCI in Table 6.2 are based on standard estimates for major additions to chemical processing operations at partially developed sites (Peters and Timmerhaus 1991). Table 6.2 provides information on the ranges of typical ratios for major plant additions to an existing site. The ratios used for the BCD STR system fall into the low end of these typical ratio ranges, since the system will be skid-mounted, and onsite installation activities will be minimal. Use of the ratios in Table 6.2 results in a total FCI of $310K to purchase and deploy a 300-gal BCD STR system.

Table 6.1. BCD Equipment Purchase Costs

Equipment	Year Acquired	Purchase Price	May 1996 Cost
Reactor Vessel	1991	2800[(a)]	3,000
Nickel Sheets	1991	5,100[(a)]	5,400
Electric Heating Mantle	1991	18,000[(a)]	19,000
Agitator for STR	1990	2,000	2,100
Skid for System	1991	2,300	2,400
Condensate Receiver Tank	1991	950	1,000
Cooling System for STR	*	*	47,300[(b)]
Forced Air Heat Exchanger	1991	5,200	5,500
Flexible Screw Conveyer	1991	11,000	12,000
Stainless Steel Tanks (2 - 500 gal)	1991	5,300	5,700
Agitators for Tanks (2)	1990	1,900	2,000
Pumps (3)	1990	5,400	5,700
Carbon Adsorption Units (2)	1991	1,400	1,500
Total Equipment Cost		61,000	110,000

(a) Original purchase costs for this equipment were based on a 400-gal STR vessel; these costs were scaled to a 300-gal STR using the 0.6 power rule.
(b) Cost based on recent vendor quotes.

The costs associated with service and support facilities can be significant and highly variable, depending on the site and the availability of existing facilities. While a ratio of 30% was used for this economic evaluation, if the BCD system were to be deployed at a site containing no existing facilities or utilities, a ratio of 55% may be more appropriate.

Table 6.2. Ratio Factors Used in Estimated Fixed Capital Investment Costs for 300-gal BCD STR System

Item	Percent of Equipment Cost (Typical Ranges)[a]	Percent of Equipment Cost BCD Operation
Direct Costs		
Purchased Equipment (delivered)	100%	100%
Installation	25 to 55%	30%
Instrumentation and Controls	6 to 30%	13%
Piping (installed)	16 to 66%	16%
Electrical (installed)	10 to 15%	10%
Site Preparation	10 to 20%	10%
Service/Support Facilities	30 to 80%	30%
Total Direct Costs (TDC)	197 to 366%	209%
Indirect Costs		
Engineering - 8% of TDC	16 to 30%	17%
Construction Expenses - 10% of TDC	20 to 37%	21%
Total Indirect Cost (TIC)	36 to 67%	38%
Contractors Fee at 5% TDC and TIC	12 to 22%	12%
Contingency at 10% TDC and TIC	23 to 43%	25%
Fixed Capital Investment	268 to 498%	284%

(a) Peters and Timmerhaus (1991)

6.2 Operating Costs

Annual operating cost estimates for processing 23,000 kg each of wool felt and paint chips/year are shown in Table 6.3. An operating schedule of 12 hr/day, 250 days per year was assumed. The FCI is depreciated over 10 years of operation with maintenance and repairs estimated at 5% of the FCI/year (Peters and Timmerhaus 1991).

Chemical costs are based on the annual consumption of the BCD reagents to process 45,000 kg total wool felt and paint chips per year. Chemical costs were taken from the May 20, 1996, issue of the *Chemical Marketing Reporter*. It should be noted that these chemical costs are significantly higher than actual costs paid during the Guam BCD demonstration; however, use of the *Chemical Marketing Reporter* provides a referenceable basis for comparisons.

Labor costs were estimated based on the following assumptions:

- Operating schedule: 1 shift/day; 250 days/yr
- Operating staff: 0.25 supervisors and 0.5 operators per shift (it is assumed operators can be engaged in other activities while the reactor is heating, at hold temperature, and during reactor cooling.)

6.3 Total Treatment Costs

The total annual treatment cost, given in Table 6.3, includes both FCI depreciation and operating costs. Based on the assumptions outlined, the total annual treatment cost is projected to be $540K/year for the 300-gal BCD system with a 10-year life. The unit cost for treating 45,000 kg/year of wool felt and paint chips is estimated at $11.90/kg. This estimate does not take into account the costs of obtaining any regulatory permits which may be required for treatment operations.

Approximately 40% of the total treatment costs are from chemical reagents and the disposal of the treated material. Without an extensive and expensive sampling program, it is unlikely that this cost can be reduced substantially. Removal of the Battelle proprietary reagent would result in having to increase the NaOH addition significantly and result in increasing the nominal operating temperature from 275°C to 350°C. The higher temperature would result in a longer cycle time, a higher energy consumption, and would require the use of an inert purge gas to since the system would be operating a near or above the auto-ignition temperature for the LW-110 oil.

The processing rate specified does not maximize the use of the STR system (i.e., 1 batch/day). If more waste required treatment, the process throughput could be doubled, which would improve the process economics.

Table 6.3. Estimated Costs for BCD Treatment of Wool Felt and Paint Chips (45,000 kg/yr)

Item	Unit	Unit Cost ($)	Number of units per year	Annual Cost ($/yr)
Chemicals				
LW-110	gal	2.00	2,800	5,600
NaOH	kg	2.44	26,000	64,000
Battelle Reagent	kg	3.28	43,000	140,000
BCD Group Reagent	kg	0.055	5,500	300
Granular Activated Carbon	kg	3.30	160	530
Subtotal				210,000
Disposal/Recycle Fee	gal	1.00	11,000	11,000
Utilities				
Electricity	kWh	0.10	53,000	5,300
Labor				
Supervisors	hr	30	1800	54,000
Operators	hr	25	3600	90,000
Subtotal				144,000
Supervision (20% of labor)				29,000
Maintenance Supplies 5% of FCI[a]/yr				18,000
Operating Supplies 1% of FCI[a]/yr				2,000
Plant Overhead Costs, 60% of Labor				87,000
Depreciation, 10% of FCI[a]/yr				36,000
Total Treatment Cost/yr				730,000

(a) Fixed Capital Investment (i.e., capital necessary for equipment, installation, and all auxiliaries for complete process operation) for a 300-gal BCD STR system is $310K.

6.4 Alternative Processing Strategy

Current disposal costs for wool felt and paint chips generated from PSNSY vessel decommissioning activities range from approximately \$4/kg to \$6/kg. Consequently, use of Stage 2 BCD for treatment of these streams does not appear to be economical. The test performed to evaluate the use of BCD Stage 1 for treatment of paint chips generated from shot/sand blasting activities shows that Stage 1, with and without the sodium bicarbonate catalyst, removed the PCB in the paint chips to below the TSCA treatment target.

A recent evaluation was performed that examined the economics of BCD Stage 1 and Stage 2 combined to treat PCB-contaminated soils (Schmidt et al. 1996). This evaluation gave a total treatment cost of \$400/metric ton (\$0.40/kg) for a system processing 7000 metric tons per year. If paint removal activities were accelerated at PSNSY, and the paint chip generation quantity increased substantially over the currently projected 20,500 kg/yr, use of BCD Stage 1 to treat this stream should be considered. Additionally, small-scale rotary calciners capable of processing the current paint chip waste stream are available for \$40K to approximately \$100K.

7.0 Conclusions and Recommendations

PCB-contaminated wool felt and paint chips from Navy vessel decommissioning activities at PSNSY were successfully treated in the liquid-phase BCD process (Stage 2 BCD). However, Stage 2 does not appear economical in comparison with current disposal methods.

A series of screening tests were conducted with the 2-L bench-scale STR under various conditions and reactor loadings to determine the most efficient operations for specific wastes; then the process was demonstrated in the 20-gal pilot-scale STR system. The results of these runs led to the following conclusions and recommendations.

7.1 Conclusions

Treatment of the wool felt did not require catalyst or hydrogen donor addition. It is believed that the wool felt matrix itself provides the necessary constituents for the BCD chemistry as it undergoes decomposition reactions in the presence of NaOH and heat.

Reagent addition rates appear to be driven more by the waste matrix loading than the PCB concentration in the waste matrix. The wool felt and paint chip matrices presumably tie up or consume substantial quantities of the NaOH; in turn, large quantities of NaOH must be added to treat the relatively small concentration of PCB in the paint chips. These matrix effects have an impact on the process economics.

Through use of the Battelle proprietary reagent, the reaction temperature for the BCD process was decreased from 350°C to 275°C. Furthermore, PCB concentrations were decreased from approximately 75,000 ppm to the TSCA target treatment level ($<$ 2 ppm per congener) in 1 hr at 275°C.

Materials handling problems were encountered when treating high loadings of solids (wool felt, paint chips, and reagents). Solids formed and tenaciously adhered to the walls and bottom of the STRs. Cleanout of reactor vessels required the use of a hammer and chisel to remove the deposits. If further testing is pursued, a rake must be installed on the agitator shaft near the bottom of the reactor.

PCB concentration in the feedstocks tested varied by more than 100%. As a result, for a full-scale operation, the nominal reagent loading must be conservative (i.e., more reagents than needed must be added to account for uncertainty), or an extensive sampling program will be necessary to quantify the PCB concentrations for each batch to be processed.

The liquid-phase BCD process can be conducted as an essentially closed process. Bench-scale testing showed that organic condensate can be safely recycled back to reactor for complete PCB destruction. Most other PCB destruction processes generate PCB-containing residual streams that require further treatment or disposal.

Stage 1 BCD appears to be a potentially viable method for treatment of the PCB-contaminated paint chips from shot/sand blasting activities. A test to examine the efficacy of using Stage 1, with 10% by weight sodium bicarbonate, reduced the PCB concentration from approximately 260 ppm PCB to less than 0.1 ppm total. Additionally, unassisted thermal desorption (i.e., no sodium bicarbonate addition) was effective in reducing the PCB concentration in the paint chips to less than 1 ppm total.

Although the BCD process was demonstrated to efficiently treat the PCB-contaminated material, the cost of the treatment is likely to be about twice the current cost for disposal of these materials. Current disposal costs for wool felt and paint chips are typically $4 to $6/kg. An economic evaluation of a scaled-up STR system showed that the total treatment cost, including fixed capital investment and operating costs, is about $11.90/kg. However, based on a previous economic evaluation, if a paint chip stream larger than the currently projected stream (i.e., 20,500 kg/yr) is generated, the Stage 1 total treatment cost would be about $0.40/kg.

As a result of this project, a better understanding of the BCD process chemistry has been developed. This information can be used to assist in the selection of process conditions for the treatment of other matrices.

A 1-year TSCA Research and Development Permit secured and renewed for a second year provides flexibility to examine a large number of waste streams from PSNSY for treatment of decommissioning wastes and for removal and treatment of paint from contaminated painted metal.

7.2 Recommendations

Use of BCD Stage 1 for treatment of paint chips and shot/sand blasting debris should be considered. With the current projections that 20,500 kg/yr of this stream will be generated, it is unlikely that the capital investment for a thermal desorption unit could be justified. However, if paint removal operations are stepped up at PSNSY, it is likely that Stage 1 BCD treatment of the stream, and possibly unassisted thermal desorption, would be more cost effective than the current disposal practices.

Closed-system aqueous-phase PCB destruction testing should be further investigated. Preliminary aqueous-phase testing produced promising results. Use of a completely closed system would eliminate potential concerns with process emissions.

Investigations of methods for removal of PCB-contaminated paint from painted metal components should be pursued. Metal coated with paint containing PCB or contaminated through contact with other materials containing PCB is the largest PCB waste stream generated at PSNSY. Current practices for such material include disposal in secured land fills, shot blasting, and solvent stripping. A number of other paint removal technologies should be evaluated for this waste stream. Testing with materials from PSNSY would also allow PNNL to extend its technology development efforts on PCB treatment using the BCD process. Furthermore, PNNL has a TSCA R&D permit that allows testing of the following techniques for paint removal: solvent washing, vibratory finishing, supercritical carbon dioxide cleaning, hot gas decontamination, graphite electrode DC arc furnace treatment, high-pressure washing, flashlamp technology, and electrochemical oxidation.

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Appendices

Appendix A

Description of Analytical and Quality Assurance Procedures

Appendix A

Description of Analytical and Quality Assurance Procedures

A.1 Analytical Calculations, Calibrations, and Internal Quality Control Checks

Early in the project review cycle, much effort was taken into refining the Quality Assurance (QA) plan and ensuring that proper procedures and safeguards were put in place. For this project, a method based on EPA Method 8080A (GC/ECD), with supplemental information taken from EPA Method 600/4-81-045, was used for quantification of PCB in most samples. Method 600 refers specifically to the analysis of waste oils for PCB content, and has some specific data regarding accuracy and precision of oil analyses. The tables in Method 600 have been used to provide estimates for accuracy and precision.

A.1.1 Definitions

- *Congener*: For PCBs, there are 209 distinct congeners/isomers that are identified by both the degree of chlorination (i.e., number of chlorine atoms on the specific PCB) and by the positions of the chlorine atoms on the biphenyl rings. Examples of specific congeners are 2-chlorobiphenyl (a monochlorinated biphenyl); 2,2,3,3,6,6-hexachlorobiphenyl. Not all of the individual congeners are completely resolvable on the GC/ECD with this particular program.

- *Homolog*: For PCBs, homologs refer to degree of chlorination (i.e., monochlorinated, dichlorinated, trichlorinated, etc.). Examples of monochlorinated homologs are 2-chlorobiphenyl, 2'-chlorobiphenyl, 3-chlorobiphenyl, often abbreviated as 1-CB, 2-CB, etc.

- *Primary standards*: Stock Dry Cleaning Manufacturer's Association (DCMA) solution and stock Aroclor solutions. Primary standards were stored in their original containers at 4°C.

- *Working standards*: Working standards were prepared from the primary standards by making serial dilutions. Due to the use of a four-point curve chromatograph, four different working standard concentrations were prepared. Dilutions were stored at 4°C in 1-mL injection vials.

- *Laboratory control standard (LCS)*: Standard #3 served as the LCS. After every 10 samples were injected, Standard #3 was injected to verify the stability of the GC/ECD system.

- *PCB locator mixture*: The DCMA standards served as the PCB locator mixture.

A.1.2 GC/ECD Method for PCB Quantification

The PCB concentration was calculated on a mg/kg basis, using commercial mixtures of PCB as standards. The analysis time, not including data reduction, was approximately 1 hr/sample, including the time for the GC to cool down and reset for the next sample. The samples were diluted on a weight/volume (W/V) basis.

The ECD is specified for use with this method. Sensitivity of the PCB analysis with this detector is often affected by interferences in the sample matrix. For this reason, Florisil cleanup and/or acid/permanganate cleanup methods were required for acceptable results.

A.1.2.1 Apparatus

Gas Chromatograph: Hewlet Packard Model HP 5890 Series II GC equipped with automatic pressure control and on-column 1/4-in. injector. System is coupled with a 100-station autosampler.

Detector: Electron Capture Detector

Column: 30 m x 0.25 mm-ID fused silica capillary column coated with DB-5 at 0.25 micron

Carrier Gas: Helium at 30 cm/sec flow rate, nitrogen (purge)

Injector: Splitless injection by autosampler. Sample injection quantity is 2 μL.

Injector Temperature: 300°C

Detector Temperature: 310°C

Temperature Program: 40°C isothermal for 5 min, 25°C/min to 180°C, 5°C/min to 300°C, and hold for 10 min before cooling down. PCB elution occurs from about 180°C to 280°C.

A.1.2.2 Reagents

Carrier Solvents: hexane or isooctane; acetone for extraction of solid samples

Calibration Standards: Principal standard for PCB was DCMA standard PCB mix. The following Aroclor standards were used as needed for quantification of feed material: Aroclors 1254, 1260, 1268, and DCMA standard. Certificates on the analyses of the standards were maintained in the project records.

DCMA PCB Analytical Standard - Stock Solution

PCB Isomer	Concentration
2-chlorobiphenyl	100 μg/mL
3,3-dichlorobiphenyl	100 μg/mL
2,4,5-trichlorobiphenyl	10 μg/mL
2,2,4,4-tetrachlorobiphenyl	10 μg/mL
2,3,4,5,6-pentachlorobiphenyl	10 μg/mL
2,2,3,3,6,6-hexachlorobiphenyl	10 μg/mL
2,2,3,4,5,5,6-heptachlorobiphenyl	5 μg/mL
2,2,3,3,4,4,5,5-octachlorobiphenyl	5 μg/mL
2,2,3,3,4,4,5,5,6-nonochlorobiphenyl	5 μg/mL
Decachlorobiphenyl	5 μg/mL

Aliquots of the stock solution were diluted to prepare four working standards containing concentrations of all 10 PCB homologs at the following concentrations relative to the DCMA stock solution:

Standard 1	DCMA Standard - stock solution in hexane
Standard 2	1/10 DCMA Standard - dilution in hexane
Standard 3	1/100 DCMA Standard - dilution in hexane
Standard 4	1/1000 DCMA Standard - dilution in hexane

A calibration curve was prepared for each batch of analytical samples injected on the GC using dilutions of the stock calibration solutions to permit concentrations from 0.1 to 100 ppm of the monochlorobiphenyl to be quantified (Exhibit 1 in Attachment 1). Individual single congener peaks that exceed the calibration limit of their homologs were appropriately diluted to bring the concentrations within the calibration curve. In some cases the same sample had to be run at two dilutions to effectively measure the concentrations of all 10 homologs. For each batch of samples processed, all calibration standards were run at the beginning of the batch. An additional standard mix was often injected during the batch to verify consistent recovery.

A.1.3 Calculation of PCB Concentration Using GC/ECD Method

Each peak on the sample chromatograph between 2-chlorobiphenyl and decachlorobiphenyl retention times was assumed to be a PCB. Each peak was identified and quantified as a specific homolog, depending on its retention time relative to the 10 standard homologs in the DCMA mix. A point was chosen midway between each standard homolog, and each peak was assigned a homolog that was bracketed within. Each peak was then quantified using the calibration curve of its specific homolog assignment.

Through multiple injection of various working standards in the expected calibration range, it was found that the response factor for the various PCB homologs was effectively linear, for analytical purposes, between two points on the analytical calibration curve in the three highest standards; and for the lowest standard, the response area from the ECD slightly tapered off . Thus, it was decided that the most expedient method for calculating the PCB concentration within an injected sample was to calibrate the response based on a four-standard-plus blank, point-to-point linear calibration, including a clean hexane blank as the point at the origin. A spreadsheet (Exhibit 2 in Attachment 1) was devised to calculate the PCB concentrations for each peak using data from the standards, sum the peaks into the 10 homologs, and report the concentrations in μg/g of each homolog.

With each batch of samples analyzed, a set of standards was run and used to calculate new coefficients and new constants (i.e., a calibration curve was generated for each batch). This was critical since the analytical instrument used for this analysis was shared among several programs and columns were frequently changed, thereby requiring strict checks on the operability and response of a GC following adjustments or changes.

A sample calibration spreadsheet, and the results from raw data input into the calibration spreadsheet is included as Exhibit 1 in Attachment 1.

A.1.4 Generation of Calibration Curves

For each batch of samples analyzed via GC/ECD, a calibration curve was generated and used to quantify the PCB concentration for that specific batch. The 4 DCMA standard solutions were analyzed to generate the curve. Because the standard solutions contain 10 specific congeners representing the 10 homologs, 10 peaks were generated for each standard. Point-to-point linear calibration was used in a spreadsheet as detailed in Section A.1.3.

From this linear regression, a coefficient and constant were determined for each homolog. The linear regression was performed with a spreadsheet. A sample calibration spreadsheet is included in Attachment 1 as Exhibit 1. For each batch of samples, a copy of the corresponding calibration spreadsheet was generated and maintained with the data from the batch.

Running the standards also generated retention time data for the standard homologs. A point was chosen midway between each standard homolog to create 10 retention time intervals for assigning a homolog classification for each PCB peak generated from a sample chromatograph. Homolog retention time intervals were also provided on the calibration spreadsheet.

A.1.5 GC/ECD Operations

A batch of samples was run for every one or two experiments performed and consisted of approximately 10 to 40 sample extracts (including various dilutions), depending on the time and availability of the GC. The samples extracts along with standards and blanks were loaded into the tray of the autosampler for each batch and left to run overnight, and sometimes multiple days.

Each batch of samples was run on the GC/ECD as described below.

1. At the beginning of every program (for each batch) inject 4-μL hexane blank with the column bake-out temperature program and repeat. These two bake-out cycles will clean the column of any residual material to establish a reproducible baseline. Bake-out temperature program is as follows: "Inject at 40°C, hold 2 min, 15°C/min to 310°C, hold at 310°C for 10 minutes."

2. Analyze the blank—hexane. Inject 2-μL hexane blank using the standard analytical temperature program.

3. Analyze the four working standards (2 μL injections) for a 4 pt. curve. Analyzed the standards in the following order: Standard #1, Standard #2, Standard #3, and Standard #4.

4. Analyze the blank—hexane.

5. Analyze 5 unknown sample extracts. Inject and analyze one unknown twice.

6. Analyze the blank—hexane.

7. Analyze 5 unknown sample extracts.

8. Analyze the blank—hexane.

9. Analyze the LCS (i.e., Standard #3)

10. Repeat Steps 5 through 9 until all samples have been analyzed.

For the calibration curve, a four-point concentration curve was used. A range of known PCB concentrations were prepared and analyzed as working standards. One of the concentration levels was at a concentration near, but above, the method quantification limit (i.e., Standard #4)

Generating acceptable accuracy and precision for the GC/ECD method requires several activities. A solvent blank must be analyzed to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples was extracted or reagents changed, a new solvent blank was processed as a safeguard against contamination. The initial solvent blank injections following the column bake-out indicate if any contamination has reached the working solvent bottles. Further injections will indicate if any material is being hung up on the column or injector from samples being injected at a PCB concentration that is too high. This was used in addition to visual analysis of each chromatogram, to determine if a sample needed to be marked as suspect or rejected if it was injected in the same set as a blank showing carryover from previous samples.

For 1 in every 5 experimental runs, the percent total recovery was monitored in duplicate. The samples were collected and split, with one split being spiked. Both the spiked and unspiked samples were extracted and analyzed to determine the total percent recovery.

A.2 Sample Data Handling

For each sample analyzed, for PCB peaks, electronic data were generated on the peak height, peak area, and peak retention time. The chromatograph for each blank, standard, and sample was examined to determine its integrity (i.e., carryover from samples, peaks being clipped, smeared peaks, stability of baseline). After the chromatograms were verified, the peak area data were sorted by homolog and entered into a spreadsheet. An example of the data spreadsheet is included as Exhibit 2 of Attachment 1. The peaks were divided into homologs in groups relative to the 10 PCB standards in the DCMA standard mix, and were then quantified in accordance with the calibration set. Final reports were then generated from each batch, including summation of each of the 10 homologs for each sample, sample name, analysis order, and notes regarding quality, usability, and problems observed in the chromatogram as it was interpreted. Exhibit 3 of Attachment 1 is the sample final reporting output following the quantification. For each batch analyzed a spreadsheet equivalent to Exhibit 3 was generated.

A.3 Analytical QA Reporting

The information provide here describes how each of the QA points established at the beginning of the project were addressed and also covers problems and interferences in the analytical method, how they were discovered, and what corrective action was taken.

A.3.1 QA Compliance Reporting

Much effort was placed in creating a set of acceptable QA standards and checks for the analytical procedures used in this evaluation. A set of standards were developed to supplement normal operational and analysis procedures to ensure the generation of quality data. The QA checks that were put into the analytical procedure are listed below.

Frequency of Data Quality Indicator Checks

Data Quality Indicator	Frequency
Precision	
RPD for GC/ECD	1 per 10 Injections
RPD for Total Method	1 per 5 Runs
Accuracy	
% Recovery - Total Method	1 per 5 Runs
Method Quantification Level	
GC/ECD	1 per Batch
Total Method	1 per 5 Runs
Blanks	
GC/ECD	1 per 5 Injections
Total Method	1 per 5 Runs

A.3.2 Precision

For precision calculations of the GC/ECD, the duplicate samples gave an estimate of overall precision by calculation of relative percent difference (RPD). The overall method precision of the laboratory analysis was determined by subtracting the two values V1-V2, multiplying this number by 200, and dividing the result by the sum of the two values V1+V2. The actual RPD is an absolute value.

$$RPD = [(C_1 - C_2) \times 100\%]/[(C_1 + C_2)/2]$$

where RPD = relative percent difference
C_1 = larger of two observed values
C_2 = smaller of the two observed values

For every 10 sample extracts analyzed, one was injected and analyzed twice to allow for routine determination of precision of the GC/ECD.

On average, RPDs ranged from 4% to 12%, and the calculated average included outlying values attributed to quantifying isomers that were at or below the lowest PCB standard (1/1000 DCMA mix) and on the edge of the detection limit. Precision of double-injected samples was one of the means for determining when the GC column needed to be replaced or adjusted.

Relative Percent Deviation for GC/ECD and Entire Analytical Method

Homolog	**RPD for GC/ECD**	**RPD for Method**
1-CB	11%	20%
2-CB	8.5%	8.0%
3-CB	6.3%	16%
4-CB	4.5%	5.5%
5-CB	7.3%	11%
6-CB	6.6%	21%
7-CB	7.4%	13%
8-CB	8.5%	9.0%
9-CB	9.5%	5.4%
10-CB	12%	12%

Precision for the entire method (i.e., extraction and analysis) was determined for the critical parameters once every fifth run. This was accomplished by extracting and analyzing a sample twice and comparing the results. On average, RPDs ranged from 5% to 21% for each homolog.

A.3.3 Accuracy

Accuracy of the data was determined by comparing the actual sample with a spiked sample and accounting for the amount of the spike. Sample accuracy is calculated as the fraction of spike recovered in the analysis as follows:

$$\%R = 100\% \times [(S - U)/C_{sa}]$$

where $\%R$ = percent recovery
S = measured concentration in spiked sample
U = measured concentration in unspiked sample
C_{sa} = actual concentration of spike added

Accuracy for the entire method (i.e., extraction and analysis) was determined for the critical parameter once every fifth run. This was accomplished by splitting a product sample and spiking one split. Both splits were extracted and then analyzed.

Analysis of spiked samples indicated the deviation from expected recovery as shown below. The one outlying value, standard deviation for 3-CB recovery, is reported for completeness but was due entirely to a single outlying sample spiked with a lower-than-usual spike, nearly at the homolog detection limit. Performing recovery and standard deviation calculations for the 3-CB set without this sample yielded a value of 86% recovery with a standard deviation of 18%.

Method Accuracy—Recovery and Standard Deviation

Homolog	Average Recovery	Standard Deviation
1-CB	111%	23%
2-CB	99%	21%
3-CB	117%	65%
4-CB	91%	17%
5-CB	107%	23%
6-CB	96%	7%
7-CB	107%	12%
8-CB	116%	21%
9-CB	128%	35%
10-CB	121%	22%

Overall since average recoveries were greater than 100%, reported data and PCB destruction efficiencies are conservative.

A.3.4 Method Quantification Level

To meet the project objectives, it was necessary to be able to accurately determine the PCB concentration to 0.5 ppm per congener in the treated product. Accordingly, with each batch of samples run, a low concentration standard was injected that contained a 1 to 1000 dilution of the DCMA standard (see Section A.1.2.1).

At a dilution of 1 to 1000, the standard contained 0.1 μg/mL of both mono- and dichlorobiphenyl. Based on significant previous BCD testing, mono- and dichlorobiphenyl are the two homologs most difficult to destroy (i.e., most likely to be found during unsuccessful treatment). Therefore, for each batch it was demonstrated that the instrument was capable of accurately resolving these homologs at this concentration prior to initiating actual sample analysis. In the cases where the analysis was not able to detect the dilution of the DCMA standard, the series was halted and the GC column fittings were adjusted and tightened. Further corrective action consisted of increasing the injector volume from 2μL to 4μL.

Compliance for the detection of the 1/1000 DCMA standard was met in all analytical runs with the exception of the batches tested on 6/23/96 and 7/8/96. Due to column degradation, these two sets were only able to resolve the 1/100 DCMA standard, while all peaks of the 1/1000 standard were not resolvable. For these batches, the LCS, and thus the minimum detection limit, was redefined as the 1/100 standard. Thus, samples with homolog concentrations below the 1/100 DCMA standard were rejected and reanalyzed at a later time. Samples with concentrations above the 1/100 DCMA standard were accepted as falling above the detection limit. The samples tested over these two analytical runs were primarily from Runs PR1, PR2, and PR3. PR1 and PR2 did not have any samples that approached the detection limit. PR3 had treated product that was below the detection limit for the analytical batch, and the failing samples were rejected and reanalyzed in the 8/22/96 batch.

A.3.5 Analytical Blanks

To verify the column is cleaned out, and that a consistent baseline has been established, PCB-free blanks were frequently injected. Before a batch of samples was analyzed, the column was baked out with blanks to verify that the column was cleaned. Additionally, after every 5 sample injections, a blank was injected. This was critical in ensuring that there was no carryover and residual PCB or other material left in the column or injector between injections. Samples analyzed around a blank or other sample that showed carryover were labeled as invalid and injected again where possible.

To verify that false positives are not occurring and that the extraction and analysis techniques have not been compromised, a field blank (clean sample of oil) was extracted and analyzed once for each five runs. This was the primary mechanism for confirming a detectable non-PCB peak set existed across the 1-CB range. Early in the analytical operations for this project, it was noted that both the chromatograms for extracted LW-104 and LW-110 oil taken directly from the manufacturer and oil samples from theoretically treated BCD tests using LW-104 and LW-110 oil as a primary medium displayed compounds that eluted in the range of 1-CB homologs. The artifact is referred to as the "4-peak" contamination as it consisted of four primary observable peaks with a two subsidiary peaks, 5 of which eluted between standard elution times for 1-CB and 2-CB, and thus were quantified as 1-CB homologs. The final two subsidiary peaks were not always observable, depending on the condition of the column and analytical equipment. The table below depicts the peaks detected in a

LW-110 chromatogram and a typical BCD treated sample (R1-8). Note that the area response is "as injected" and does not reflect the actual sample concentration due to the standard 1:10 dilution in the Florisil extraction procedure.

LW-110		**R1-8BF**		**DCMA Standard 1/100**	
Ret. Time (min)	Area	Ret. Time (min)	Area	Ret. Time (min)	Area
11.822	49921	11.829	55928		
12.186	40211	12.196	24687	12.164 (1-CB)	89668
12.537	16532	12.551	19064		(10 ppm)
12.643	42891	12.658	31217		
12.910	11929	13.024	18567		
13.402	18794	13.421	16569		

The extraction of a hexane solvent blank using the Florisil method did not produce the artifact; thus, the non-PCB contamination was assumed to come from the LW-104 or LW-110. Use of hand-made Florisil extraction columns and the acid/permanganate liquid/liquid extraction cleanup techniques did not eliminate the artifact, and steps were taken to account for the interference. In the analytical sets where a field oil blank was run in parallel with the samples, it was used as a reference for determining how much of the detected signal in treated samples was due to this artifact. This was not a rigorous solution, as product oil samples would not have the same density of this artifact potentially due to combined effects of heat degradation during the treatment process, fractionation, distillation of lighter oil components, and the diluting effect of other reagents and materials soluble in the product oil samples. Rather, a visual analysis of the ratio of the four primary peaks on the chromatogram of the artifact was performed to determine if any one of them was potentially supplemented by actual PCBs left in the product matrix. All sample values were reported without any correction including the artifact contribution, as no exact and expedient method for subtracting out the artifact contribution was available for numerical interpretation.

Appendix A - Attachment 1

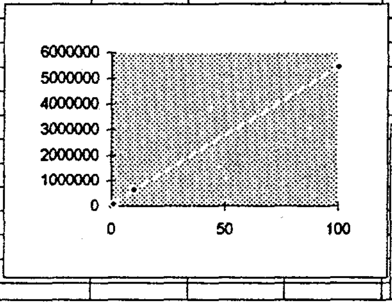
Exhibits of

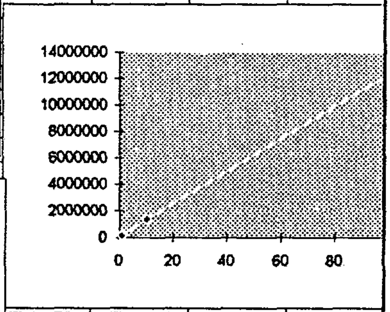
GC/ECD Calibration Calculations
Peak Area Data Spreadsheet
Final Analytical Data Output

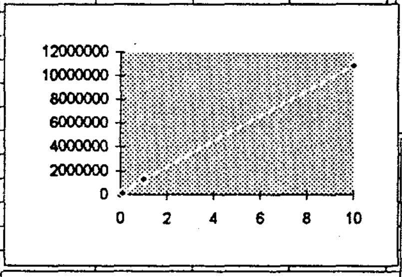
10/26/95

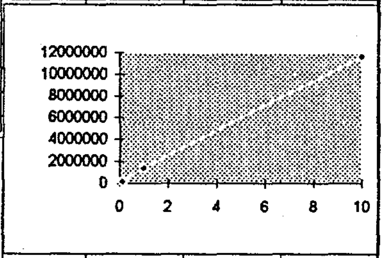
piecewise linear calibration 4 point plus origin

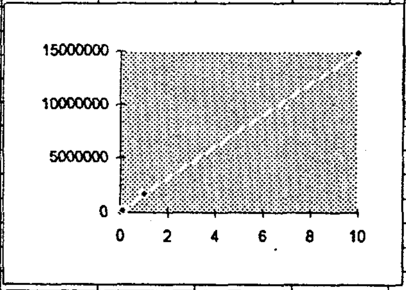
	conc	area	x
1cb	conc	area	x
	0	0	
	0.1	14942	6.69E-06
	1	89688	1.2E-05
	10	645644	1.62E-05
	100	5449788	1.87E-05
2cb	conc	area	x
	0	0	
	0.1	37572	2.66E-06
	1	192854	5.8E-06
	10	1386607	7.54E-06
	100	1.24E+07	8.18E-06
3cb	conc	area	x
	0	0	
	0.01	23951	4.18E-07
	0.1	162247	6.51E-07
	1	1343142	7.62E-07
	10	1.08E+07	9.47E-07
4cb	conc	area	x
	0	0	
	0.01	24989	4E-07
	0.1	169379	6.23E-07
	1	1418727	7.2E-07
	10	1.17E+07	8.78E-07
5cb	conc	area	x
	0	0	
	0.01	32624	3.07E-07
	0.1	207258	5.15E-07
	1	1754568	5.82E-07
	10	1.48E+07	6.88E-07
6cb	conc	area	x
	0	0	
	0.01	31061	3.22E-07
	0.1	171690	6.4E-07
	1	1376460	7.47E-07
	10	1.11E+07	9.25E-07
7cb	conc	area	x
	0	0	
	0.005	21467	2.33E-07
	0.05	163799	3.16E-07
	0.5	1784755	2.78E-07
	5	1.69E+07	2.97E-07
8cb	conc	area	x
	0	0	
	0.005	20618	2.43E-07
	0.05	168149	3.05E-07
	0.5	1692154	2.95E-07
	5	1.63E+07	3.09E-07
9cb	conc	area	x
	0	0	
	0.005	23243	2.15E-07
	0.05	152710	3.48E-07
	0.5	1700283	2.91E-07
	5	1.58E+07	3.2E-07
10cb	conc	area	x
	0	0	
	0.005	22516	2.22E-07
	0.05	138042	3.9E-07
	0.5	1335886	3.76E-07
	5	1.18E+07	4.31E-07

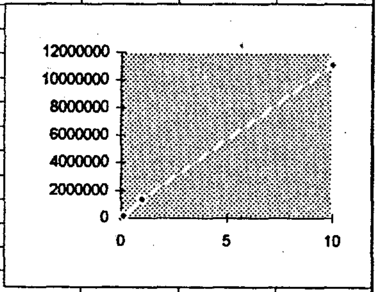


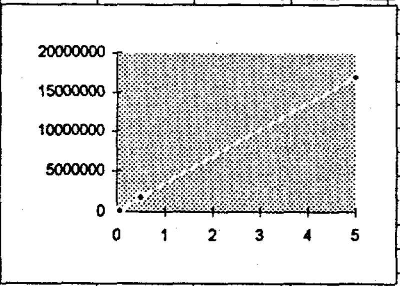


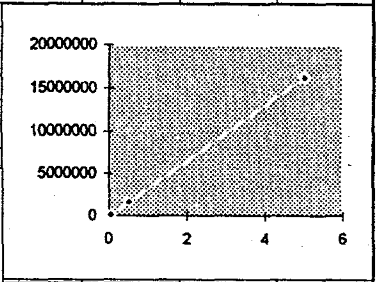


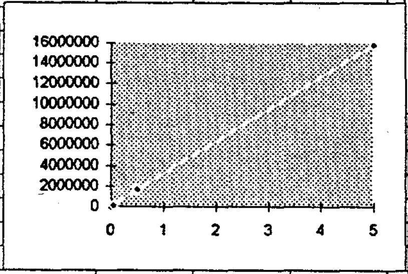












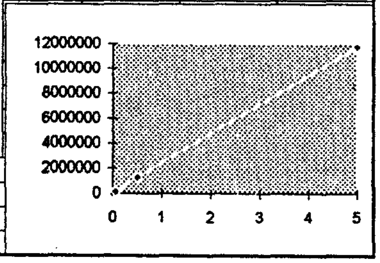


Exhibit 1. GC/ECD Calibration Calculations

	totals										
1cb	16.84276										
2cb	54.4318										
3cb	6.78013										
4cb	8.561575										
5cb	9.996459										
6cb	18.42077										
7cb	0										
8cb	0										
9cb	0										
10cb	0										
CL	area										
1cb	207254	385544	531373	0	0	0	0	0	0	0	0
2cb	729535	762353	544541	149613	3139582	2040803	0	0	0	0	0
3cb	357989	165221	1418201	3077951	1954157	1485573	0	0	0	0	0
4cb	794067	958717	2955695	1362744	554196	1361968	485147	2979477	0	0	0
5cb	410060	1010218	313426	156969	893217	4902955	625087	4041996	3776286	0	0
6cb	829790	371259	443705	1314778	1974152	1346540	1993384	1050090	4262320	5295554	3721043
7cb	0	0	0	0	0	0	0	0	0	0	0
8cb	0	0	0	0	0	0	0	0	0	0	0
9cb	0	0	0	0	0	0	0	0	0	0	0
10cb	0	0	0	0	0	0	0	0	0	0	0
	conc										
1cb	2.903197	5.789415	8.150143	0	0	0	0	0	0	0	0
2cb	5.046171	5.293594	3.651456	0.749379	24.33973	15.35147	0	0	0	0	0
3cb	0.249182	0.102267	1.071117	2.643692	1.578923	1.13495	0	0	0	0	0
4cb	0.55001	0.66862	2.349299	0.959671	0.377213	0.959112	0.327472	2.370178	0	0	0
5cb	0.217961	0.567045	0.161753	0.074083	0.498991	3.167277	0.343032	2.574613	2.391704	0	0
6cb	0.591621	0.249084	0.303204	0.953922	1.552995	0.977649	1.570789	0.756192	3.670049	4.626015	3.16925
7cb	0	0	0	0	0	0	0	0	0	0	0
8cb	0	0	0	0	0	0	0	0	0	0	0
9cb	0	0	0	0	0	0	0	0	0	0	0
10cb	0	0	0	0	0	0	0	0	0	0	0
Residence Time Splitting chart											
	1/1	1/10	1/100	1/1000	avg						
1	12.2125	12.202	12.206	12.2053	12.20645						
2	15.2325	15.204	15.205	15.2083	15.21245						
3	16.383	16.379	16.382	16.38	16.381						
4	18.0845	18.081	18.083	18.0803	18.0822						
5	19.9955	19.992	19.993	19.989	19.99238						
6	21.792	21.789	21.79	21.7847	21.78893						
7	25.5485	25.545	25.544	25.5377	25.5438						
8	29.817	29.815	29.813	29.8067	29.81293						
9	31.033	31.03	31.029	31.0153	31.02683						
10	32.013	32.01	32.009	32.0017	32.00843						

Exhibit 2. Peak Area Data Spreadsheet

8/22/96									x				
run #	1	2	3	4	5	6	7	8	9	10	11	12	13
vial #	1	1	2	3	4	5	1	6	7	8	9	10	10
inj #	1	2	1	1	1	1	1	1	1	1	1	1	1
seq line	1	1	2	2	2	2	3	4	4	4	4	4	5
sample	hexane 1	hexane 1	std 0822 1/1	std 1/10	std 1/100	std 1/1000	hexane 1	0-Cl std	PR3-6FA	R20-6F	R20-5F	R20-8F	R20-8F
comment	a	b	c	c	c	c	d	e		f	f	f	f
1cb	x	x	x	x	x	x	0	0	0.28028	2.17234	3.42202	3.98924	4.64339
2cb	x	x	x	x	x	x	0	0	0.07573	28.7945	24.0714	25.0722	29.8072
3cb	x	x	x	x	x	x	0	0	0.02269	2.69281	1.99725	1.84662	2.39889
4cb	x	x	x	x	x	x	0	0	0.12704	2.25567	1.76614	1.46972	1.92697
5cb	x	x	x	x	x	x	0	0	0.08551	0.05182	0.04074	0.03222	0.03658
6cb	x	x	x	x	x	x	0	0	0	0	0	0	0
7cb	x	x	x	x	x	x	0	0	0.00304	0	0.00511	0	0
8cb	x	x	x	x	x	x	0	0	0	0	0	0	0
9cb	x	x	x	x	x	x	0	0	0	0	0	0	0
10cb	x	x	x	x	x	x	0	0	0	0	0	0	0
total	0	0	0	0	0	0	0	0	0.5943	35.9672	31.3026	32.41	38.813
inj dilution													
prep vol													
original wt													
final conc	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
all in ug/ml													
comment key													
RQ	ReQuantify (increase det limit)												
DRS	Dilute and ReShoot												
a	blow through blank, at start of run for cleaning												
b	blow through blank, acceptable baseline												
c	standard used to calibrate this run												
d	check blank												
e	everything in range is PCB method												
f	trashed via "PCB contaminant drag" at high florisil loading												
g(n)	n is the #cb suspected of peak saturation (must reshoot at dilution), otherwise fine												
h	blown, constant overloading, climbing baseline												
i	checked standard												
j	uncleaned sample, total mess												
k	contaminant												
l	quantified using DCMA standard congeners only												
m	blank shows overload carryover from previous sample												
n	shows "porcupine contaminant" (florisil method suspect) from 25 minutes onward												
o	Blown from carryover from previous sample												
p	Potential Blank contamination? (injector/septa back contam?))							at 19.3					
(n)X	sample injected at n times nominal standard volume (2ul)												
q	std too low for quant/ too much tailing												
r	4 peaks in mono area from oil contamination (4peaks)												

Exhibit 3. Final Analytical Data Output

Appendix B

Basis for Scaled-up Economic Evaluation of BCD Treatment System

Appendix B

Basis for Scaled-up Economic Evaluation of BCD Treatment System

An economic assessment of a scaled-up process is provided here. The bench-scale and pilot-scale testing on the PSNSY vessel materials demonstrated the efficacy of the BCD process for treatment of wool felt and paint chips but also revealed some operational difficulties associated with treating solid streams in the liquid-phase BCD Stage 2 process. The economic assessment makes the assumption that these difficulties, associated with solids precipitation and accumulation, will be addressed in the design of the full-scale STR, particularly in the design of the agitation system.

B.1 Sizing Basis for BCD System

The basis for sizing the scaled-up system is information provided in a Sources Sought Announcement (SSA) published in the Commerce Business Daily (CBD). This announcement, "SSA for the Removal and Detoxification of PCB Contaminated Material During Ship Recycling (CBD Code 272311)," with responses due by June 14, 1996, was issued by the Navy. The purpose of this SSA was to seek information on technologies for removing, processing, and detoxifying material contaminated with halogenated organic compounds (primarily PCB) and heavy metals that are generated during ship recycling operations at Navy shipyards, in particular, PSNSY. Within this SSA, information was provided on the approximate annual quantities of materials generated. The SSA indicated that 1.2 million kg of aluminum and steel plates with wool felt were generated annually. No breakout between metal and wool felt was provided; however, for the purposes of this report, based on conversations with staff from PSNSY, it has been assumed that 2% of the 1.2 million kg is wool felt (25,000 kg). Additionally, the SSA also stated that approximately 20,500 kg of paint chips and debris are generated annually. Based on these numbers, the BCD STR system was conceptually designed. Both the capital and operating costs for this system have been estimated, as discussed in Section 6.0. Although the wool felt and paint chips streams comprise a relatively small fraction of the total PCB waste volume currently generated at PSNSY, it would be possible to couple the BCD process with a paint removal/stripping process for final treatment of the residual.

The proposed process flowsheet for BCD treatment of wool felt and paint chips is based on a 300-gal STR. If the resulting processing rate is not sufficient to meet PSNSY needs, multiple parallel units could be operated. The basis for the 300-gal size is that it is a size that will allow processing of all of PSNSY wool felt and paint chip debris at a processing rate of one run per day. Furthermore, the 300-gal size is near the size of the unit demonstrated in Guam, and all components for that size can be procured off the shelf.

B.2 Operating Strategy for 300-gal STR

Based on bench-scale testing with wool felt and paint chips, and full-scale BCD testing in Guam, a skid-mounted STR system would consist of an electrically heated 300-gal reactor; a liquid and solid feeding system; an air-cooled condenser; and a closed-loop, air-cooled cooling system. Ancillary support equipment would include a covered storage area for reagents.

The reactor would be loaded with paint chips/wool felt via hopper and screw conveyer. Solid reagents would also be added to the reactor via screw conveyer. The reaction medium, a high-boiling-point oil would be pumped into the reactor either directly from 55-gal drums or from an oil storage tank. After the waste and reagents are added, the reactor would be sealed and the heating cycle initiated. During the course of the treatment cycle, any organic and aqueous condensates generated would be collected in the condensate receiver tank. After operating at the target reaction temperature for the necessary time, the internal cooling coils would be engaged to reduce the temperature of the contents to near-ambient conditions. The reactor would be pumped out (either into drums or a storage tank). The organic condensate (most likely containing some PCB would be used to make up a portion of the reaction medium oil for the next run. Recycle of organic condensate has been extensively tested and demonstrated with BCD treatment of wool felt and paint chips during bench-scale testing in this project. During the fourth pilot-scale run, 96% of the oil added to the feed initially was recovered for potential reuse. For the full-scale system, it is assumed that 90% of the oil would be recovered after each run.

B.3 Process Footprint

A 300-gal BCD system would fit on a single 2.1 m x 5.5 m skid. The 400-gal STR system demonstrated on Guam occupied a single skid of this size.

B.4 Basis of Reagent Addition and Operating Conditions

Data from the third and fourth pilot-scale runs (PR3 and PR4) in this project were used for guidance in selecting nominal operating conditions and reagent loadings. Table B.1 shows the key ratios for reagent additions in these two runs. Although PR4 was conducted at a higher NaOH:PCB mass ratio than PR3, PR3 more effectively reduced the PCB concentration at lower temperatures. In examining the analytical data from PR4, it would appear that the system ran out of base. Several differences that may have adversely affected PR4 include the addition of the paint chips (and spent steel shot blast) to the matrix; use of LW-110 vs. LW-104 as the reaction medium; and the lower ratio of NaOH:total waste in PR4. Examining these differences in light of the results from the bench- and pilot-scale testing indicates that the NaOH:total waste ratio most likely had the greatest effect as a result of the matrix consuming or tying up the NaOH. Therefore, as a conservative design basis for the full-scale system, the NaOH:total waste ratio will be the key parameter to set the reagent loading.

Table B.1. Reagent Loading Ratios for Pilot-scale Runs

Parameter Mass Ratio	PR3	PR4
NaOH:PCB	1.8:1	2.9:1
Battelle Reagent:PCB	2.8:1	4.7:1
BCD Group Reagent:NaOH	0.1:1	0:1
NaOH:Wool Felt	0.58:1	0.56:1
Battelle Reagent:Wool Felt	0.94:1	0.92:1
NaOH:Total Waste	0.58:1	0.28:1
Battelle Reagent:Total Waste	0.94:1	0.46:1
Reaction Oil:Wool Felt	3:1	4:1
Reaction Oil:Total Waste	3:1	2:1

Using the mass of the total waste, rather than the mass of PCB, for setting reagent loadings is in keeping with the results from the bench-scale and pilot-scale testing. To a large extent, conditions for successful treatment were found to be independent of the PCB concentration. Also use of this ratio eliminates the need to determine the PCB concentration for every batch.

During the cleanout operations following PR3 and PR4, removal of solids was found to be difficult. Therefore, for the design basis, the BCD Group reagent will be added at 20% of the NaOH loading, as recommended by staff from BCD Group, Inc.

B.4.1 Material Balance Information

STR Volume	300 gal
Operating volume	~200 gal
Waste Form	Wool felt (350,000 ppm PCB) Paint chips (500 ppm PCB)

Waste loading	91 kg wool felt 91 kg paint chips
Reaction Oil Medium	360 kg (110 gal, Sp Gr = 0.86) LW-110
NaOH	100 kg
Battelle Reagent	170 kg
BCD Group Reagent	21 kg
Mass of Batch	820 kg

B.4.2 Residual Generation

Recoverable Oil	330 kg (100 gal) (90% recovery)
Aqueous Condensate	23 kg - 6 gal (approx. 2.9% of batch[a]) PCB concentration ~ 100 ppm
Organic Condensate	11 kg - 10 gal (approx. 1.3% of mass of batch[a]) PCB concentration ~5000 ppm
Residual Solids	330 kg (42 gal); density = 2 g/cm^3

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[a] Based on pilot-scale test data with paint chips and wool felt from PSNSY.

Organic condensate would be mixed with the feed for the next run. Aqueous condensate would be polished with granular activated carbon (GAC). Upon loading of the GAC, the GAC could be dried and processed with the contaminated feed. Treatment of GAC loaded with PCB was demonstrated as part of the BCD demonstration in Guam.

B.4.3 Processing Cycle

One batch would be processed in each 24-hr day. However, the system would have the capability of treating two batches per day. At one batch per day, the waste throughput will be 91 kg/day wool felt and 91 kg/day paint chips. Each processing cycle (on a 12-hr basis) would consist of the activities described below:

Reactor loading	1 hr
Heating (to 275°C)	4 hr

Hold Time (at 275°C)	2 hr
Cooling (from 275°C to ~100°C)	4 hr
Pump out	1 hr
Total Cycle Time	12 hr

B.4.4 Utility Requirements

The utility requirements for the system were estimated for each batch processed (including heating, cooling, pumping, and operation of cooling fan motors). During reactor heatup, 820 kg of contents and a reactor vessel (estimated to have a mass of 590 kg of steel) are heated from 25°C to 275°C. Assuming specific heats of 0.5 and 0.12 cal/g-°C for the slurry and the steel, respectively, approximately 170 kW-hr will be required (with 25% loss) for the heating cycling. After agitator and pumps are accounted for, the total utility requirement will be about 40 kW during the 4-hr heating cycle. Therefore, a 50-kW service should be provided. After cooling and energy losses while at temperature are accounted for, each batch is estimated to require 210 kW-hr.

Appendix C

Analytical Data

Run 1 Report													
sample	RF1F	R1-1	R1-3	R1-4	R1-4	R1-5	R1-5	R1-6	R1-7	R1-7	R1-8	R1-8	R1-2
temp	dry feed	250	250	250	250	300	300	300	350	350	350	350	cond
time@T	wool only	0	1	2	2	1	1	2	1	1	2	2	oil
A. Date	10/30/95	10/30/95	10/30/95	10/26/95	1/7/96	10/26/95	1/7/96	10/26/95	10/26/95	1/20/96	10/26/95	1/20/96	1/7/96
type	soild samp	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	220.2822	23.03267	28.38385	0	24.78013	64.51912	72.9927	75.91775	7.831499	0.725029	10.04788	0	264.2056
2cb	1422.971	219.0815	266.9929	218.387	189.1015	830.2008	863.8177	805.3411	0.365742	0	0.439157	0	670.1364
3cb	344.1681	62.02212	86.71676	80.30575	103.3104	151.1625	#VALUE!	104.8297	0	0	0	0	73.58458
4cb	359.7317	112.3841	374.2407	#VALUE!	638.7232	>273.6	#VALUE!	176.0033	0.211372	0	0.210939	0	139.7941
5cb	298.2815	297.8231	1697.075	#VALUE!	1797.176	85.12417	60.89233	8.802713	0.158489	0	0.295035	0	119.7608
6cb	525.862	4882.389	4472.521	#VALUE!	4117.283	18.4188	11.8956	5.916112	0.364849	0	0.569688	0	324.8763
7cb	13606.94	5599.35	265.478	132.2818	139.6037	16.27122	15.62914	9.104517	1.428169	0	1.194427	0	452.5026
8cb	68978.27	941.1606	40.76648	#VALUE!	19.32745	33.94026	39.03147	23.59171	2.441154	0.049341	1.872188	0	413.7663
9cb	45619.84	36.53153	26.88975	#VALUE!	24.07248	39.59766	58.51879	32.99015	1.51932	0.064956	1.037218	0	84.83336
10cb	12046.77	6.701442	13.31125	#VALUE!	15.17766	6.694479	33.09522	4.518184	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	143423.1	12180.48	7272.375	#VALUE!	7068.555	1245.929	#VALUE!	1247.015	14.32059	0.839326	15.66654	0	2543.46
										R1-8 (2)		baseline	
worksheet										subtract		subtract	

Run 2 Report															
sample	R2-1	R2-2	R2-3	R2-4	R2-4	R2-5	R2-5	R2-5	R2-6	R2-6	R2-7	R2-7	R2-8	R2-9	R2Rinse
temp	250	250	250	300	300	300	300	300	350	350	350	350	oil and aq	350	postrun
time@T	0	1	2	1	1	2	2	2	1	1	2	2	cond.	2	glass rinse
A. Date								3/16/96		1/20/96	1/7/96	1/20/96	NA	11/20/95	11/20/95
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean		oil clean	absolute
1cb	29.58508	45.90043	86.3645	6.47023	1.812595	6.491301	4.370775	7.496577	6.531437	0	10.98254	0		8.349879	82.6522
2cb	279.2882	1380.907	1852.64	0	0	0.333423	0	0.576428	0	0	0	0		0.442941	207.3335
3cb	88.47941	515.1376	468.3359	0	0	0	0	0	0	0	0	0		0	43.13488
4cb	605.814	1201.623	618.5105	0.101116	0	0	0	0.047545	0.139788	0	0	0		0.066108	60.98378
5cb	2170.403	163.4592	58.83526	0.097967	0	0.097514	0	0	0.04299	0	0	0		0.046909	34.00412
6cb	4995.897	30.8669	19.73177	0.054857	0	0	0	0	0.292222	0	0	0		0	89.70913
7cb	165.0912	13.6923	19.15765	0.171767	0	0.032453	0	0.416398	0	0	0	0		1.143195	77.5215
8cb	33.36316	59.17345	54.73032	0.032187	0	0.029724	0	0.099495	0	0	0	0		2.279291	154.533
9cb	27.52349	101.1504	68.77483	0.030027	0	0.032562	0	0	0	0	0	0		0.858205	99.40274
10cb	22.61132	59.99766	7.51261	0	0	0	0	0	0	0	0	0		0.157561	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g		ug/g	ug
total	8418.056	3571.909	3254.593	6.958151	1.812595	7.016979	4.370775	8.636443	7.006437	0	10.98254	0	X	13.34409	849.2748
				4pk@1cb	R2-6,7	4pk@1cb	R2-6,7	4pk@1cb	4pk@1cb	"blank"	4pk@1cb	"blank"		contam	
worksheet					subtract		subtract			subtract		subtract			

Run 3 Report

sample	R3-1	R3-1	R3-1	R3-2	R3-3	R3-4	R3-5	R3-5	R3-5	R3-6	R3-6	R3-7	R3-7
temp	250	250	250	250	250	300	300	300	300	350	350	350	350
time@T	0	0	0	1	2	1	2	2	2	1	1	2	2
A. Date	11/20/95	1/7/96	3/16/96	11/20/95	11/20/95	11/20/95	11/20/95	1/7/96	3/16/96	11/20/95	1/7/96	11/20/95	1/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	21.52055	27.119	21.31493	29.8163	25.74983	46.76338	58.15527	56.12346	89.18702	9.440954	15.46401	7.628797	11.09302
2cb	217.6552	172.0035	190.6654	215.427	203.3239	666.9317	770.336	880.7006	1034.004	0	0.374882	0.342604	0
3cb	#VALUE!	56.90861	56.5034	69.60758	81.95282	205.1936	190.0684	218.5515	197.1379	0	0	0	0
4cb	#VALUE!	54.30358	57.39816	241.5361	371.0035	588.3362	#VALUE!	#VALUE!	195.7757	0.116176	0	0.249932	0
5cb	#VALUE!	80.05642	79.46323	1188.192	1705.58	208.696	11.11691	11.2745	15.23971	0.095595	0	0	0
6cb	#VALUE!	1390.497	1976.87	8628.203	7039.368	48.8685	11.28029	4.49827	3.605209	0	0	0	0
7cb	#VALUE!	7080.305	9064.221	1417.229	565.1673	16.15021	11.44549	9.527433	6.432307	1.025106	0.037595	1.062784	0
8cb	#VALUE!	5058.863	5691.74	43.53133	42.90059	26.95333	24.15236	29.67632	22.90373	2.01263	0.080637	1.915425	0
9cb	#VALUE!	51.65774	29.94476	8.479072	17.76499	54.85122	38.45916	46.83577	36.02494	0.694228	0.060633	0.539302	0
10cb	#VALUE!	4.783782	0	8.950222	0	6.902322	0	25.23935	18.64324	0.289065	0	0.289411	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	#VALUE!	13976.5	17168.12	11850.97	10052.81	1869.646	#VALUE!	#VALUE!	1618.954	13.67375	16.01776	12.02825	11.09302
								contam		4pk@1cb	4pk@1cb	4pk@1cb	4pk@1cb
worksheet													
chr	1	2	3	4	5	6							

Run 4 Report											
sample	R4-1	R4-2	R4-3	R4-4	R4-5	R4-6	R4-7	R4-8	R4-9	R4EB	R4RInse
temp	120	250	cond	250	250	300	300	350	350	carbon be	glass rinse
time@T	0	0		1	2	1	2	1	2	per g carbon	
A. Date	NA	NA	NA	NA	NA	11/20/95	11/20/95	11/20/95	11/20/95	1/7/96	1/7/96
type						soild samp	soild samp	soild samp	soild samp	soild samp	absolute
1cb						29.52551	36.90302	9.358671	21.68239	0	47.06742
2cb						194.7156	211.0355	2.801556	7.713954	0	108.7899
3cb						27.86006	12.95513	0.449469	0.763527	0	22.95987
4cb						16.90924	7.755682	0.369372	0.708767	0	52.74667
5cb						0.299916	0.395562	0.281803	0.525399	0	64.09599
6cb						0.394132	0.658018	0.270523	1.484052	0	433.7439
7cb						1.626852	1.761217	1.473986	3.856154	0.006938	#VALUE!
8cb						4.047789	4.058827	2.408327	4.230158	0.013887	#VALUE!
9cb						2.39536	1.628188	1.012821	1.700133	0.009427	#VALUE!
10cb						0	0	0	0	0	16.41127
units						ug/g	ug/g	ug/g	ug/g	ug/g	ug
total	X	X	X	X	X	277.7745	277.1511	18.42653	42.66453	0.030252	#VALUE!
								terri + ovl	terri +		
worksheet								4pk@1cb	hvy overload		

Run 5 Report

sample	R5-1	R5-2	R5-3	R5-4A	R5-5	R5-6A	R5-7A	R5-7	R5-8	R5-9	R5EB
temp	130C	250	250	250	300	300	300	300	350	350	Carbon be
time@T	0	0	1	2	1	1	2	2	1	2	
A. Date	12/11/95	12/11/95	12/11/95	12/11/95	12/11/95	12/11/95	12/11/95	12/11/95	NA	12/11/95	1/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean		oil clean	soild samp
1cb	11.94002	26.5405	28.10842	28.12164	28.97574	28.77191	29.79468	33.30472		6.312285	1.54216
2cb	106.4033	177.0152	185.2381	243.2399	352.3712	334.9628	458.5288	488.9476		0	0
3cb	38.83195	52.95901	63.70374	59.35742	147.4692	152.3137	88.98288	92.17171		0	0
4cb	31.20603	72.60956	221.6064	266.6011	356.8762	342.3686	143.2648	150.3541		0	0
5cb	28.84167	114.2759	604.014	848.7569	78.81261	51.88061	9.037068	9.195812		0	0.011194
6cb	30.2579	1537.268	4656.676	4432.466	15.50177	12.18342	1.967456	4.09414		0	0
7cb	1219.909	4653.131	1946.815	789.7622	8.302007	6.092696	5.49677	6.587047		1.927906	0.031186
8cb	6929.448	3341.675	143.3159	52.13517	20.37983	17.74801	19.45763	20.13049		4.716788	0.076726
9cb	5051.869	61.04141	24.99652	22.04632	53.31532	54.42072	23.09102	24.54505		1.935815	0.03602
10cb	1349.081	5.415499	3.899247	4.178259	0	0	3.74528	3.893771		0.576105	0.00851
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g		ug/g	ug/g
total	14797.79	10041.93	7878.373	6746.664	1062.004	1000.742	783.3663	833.2244	X	15.4689	1.705797
										contam	
worksheet											

Run 6 Report									
									d= 0.87
sample	R6-1	R6-2	R6-3	R6-4	R6-5	R6-6	R6-7	R6-8	R6-9
temp	128	250	250	250	300	300	350	350	
time@T	0	0	1	2	1	2	1	2	cond
A. Date	12/11/95	12/12/95	12/13/95	12/14/95	12/15/95	12/16/95	3/16/96	12/18/95	12/19/95
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	19.30547	29.63171	34.90828	33.93181	44.72938	62.45697	1.811366	11.17594	199.7799
2cb	141.1233	189.3049	210.4262	227.1692	604.2724	828.9731	0	3.061844	460.029
3cb	34.83904	49.79357	76.89309	76.47872	196.404	171.869	0	0	54.18081
4cb	34.12385	64.82892	261.6358	441.39	621.8376	278.4836	0	0.059443	69.27937
5cb	32.4159	142.3554	1434.568	1814.391	219.417	16.02089	0	0.140632	59.78167
6cb	29.20786	3083.675	7604.815	6342.802	50.03928	3.690567	0	0.435442	81.33362
7cb	1192.841	5811.947	1017.19	454.351	13.4631	10.43394	0.25159	5.878962	125.1462
8cb	6729.748	1869.185	54.1597	56.5526	32.60642	38.29185	0	14.57799	199.6051
9cb	4897.764	52.20947	22.22773	29.0705	57.07418	65.31518	0	6.482851	61.10751
10cb	1306.985	3.436413	14.21164	6.574764	0	0	0	2.16261	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	14418.35	11296.37	10731.03	9482.712	1839.843	1475.535	2.062955	43.97571	1310.243
							4pk@1cb	hvy contam	
worksheet									

Run 7 Report									
sample	R7-1	R7-2	R7-3	R7-4	R7-5	R7-6	R7-7	R7-8	R7-8
temp	126	190	190	190	190	250	250	250	250
time@T	0	0	1	2	4	1	2	4	4
A. Date	11/20/95	11/20/95	11/20/95	11/20/95	11/20/95	11/20/95	11/20/95	11/20/95	12/11/95
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	40.11045	26.24147	27.17427	28.76583	25.88625	53.26269	67.4515	87.05832	82.85492
2cb	87.13401	125.0458	117.646	121.3654	235.0876	675.4439	757.3451	457.9841	620.7534
3cb	43.37114	66.68396	72.0364	85.09714	89.52305	213.4802	244.9691	175.0865	190.9724
4cb	35.91551	222.7588	255.0339	340.1168	494.8053	896.1698	761.4093	#VALUE!	335.6373
5cb	30.69665	581.8091	661.3771	778.1788	866.4791	826.8827	299.242	21.74386	24.11038
6cb	51.24586	4963.796	5027.967	4994.453	4381.895	536.6179	88.63836	3.489244	5.954734
7cb	1438.967	3034.572	2562.048	1925.622	1147.525	17.6388	19.92061	9.01176	10.27658
8cb	7293.801	280.3458	133.8543	59.01555	47.67729	29.175	32.66175	25.66259	29.55733
9cb	4673.682	31.08229	12.96243	18.14528	23.53851	65.40896	65.25609	30.96702	45.31217
10cb	1054.366	0	0	0	21.73564	0	0	16.40932	19.27351
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	14749.29	9332.336	8870.099	8350.76	7334.153	3314.08	2336.894	#VALUE!	1364.703
worksheet									

Run 8 Report					
sample	R8-1	R8-2	R8-3	R8-4	R8-5
temp	166	275	285	285	condensat
time@T	0	1	1	1	
A. Date	12/11/95	1/7/96	12/11/95	1/7/96	1/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	80.71593	40.22678	9.171086	10.11543	19.69725
2cb	559.2092	22.17145	2.409782	0	0.363089
3cb	180.4223	0.52116	0	0.189171	0
4cb	299.7935	0.083947	0	0.475578	0
5cb	19.25554	0.030754	0	0.348979	0
6cb	4.170868	0.02904	0	0.377116	0
7cb	6.350846	0.51738	0.055083	0.521659	0.098697
8cb	27.89946	0.238324	0.109864	0.116394	0.040624
9cb	46.4268	0	0.035357	0	0
10cb	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g
total	1224.244	63.81884	11.78117	12.14432	20.19966
			4pk@1cb	4pk@1cb	
worksheet					

Run 9 Report

sample	R9-1	R9-1	R9-2	R9-2	R9-3	R9-4	R9-5	R9-6	R9-7	R9-8	R9-9	R9-10	R9-11
temp	133	133	250	250	250	250	300	300	350	350	222	cond	final
time@T	0	0	0	0	1	2	1	2	1	2	0		product
A. Date	1/20/96	3/16/96	1/20/96	3/16/96	1/20/96	12/11/95	3/16/96	12/11/95	1/20/96	12/11/95	1/7/96	NA	1/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean		oil clean
1cb	35.49668	48.00587	31.91879	44.0239	32.76842	40.13386	52.52561	61.43896	102.9273	171.006	224.5806		181.7584
2cb	124.7485	186.7067	210.3392	231.7249	242.6692	571.2815	1183.022	1593.589	1858.03	2361.378	2098.449		1775.818
3cb	32.49615	51.35868	57.09979	69.4739	182.8655	365.205	727.1576	675.5594	299.203	226.3148	139.4098		185.2294
4cb	23.06147	38.98987	111.3602	127.581	1234.313	2099.851	2275.69	1704.229	312.6181	143.2088	111.7754		126.9631
5cb	24.67726	33.32257	#VALUE!	733.596	1669.401	1512.089	238.8883	167.52	2.519242	1.448615	1.881156		2.393484
6cb	24.5324	48.1522	#VALUE!	10044.48	838.7295	425.0324	12.87456	16.66714	5.57833	3.066206	2.658372		4.497982
7cb	#VALUE!	1987.003	#VALUE!	4123.369	18.40761	29.07363	11.61449	10.89267	10.53353	7.70638	12.55433		11.7276
8cb	#VALUE!	9892.642	87.65133	70.19575	30.17073	27.71793	24.1655	39.32604	31.52189	21.9679	38.36682		41.66223
9cb	#VALUE!	#VALUE!	24.58819	7.731303	27.80662	72.74844	87.41047	102.029	37.45956	16.72175	38.39021		27.89239
10cb	#VALUE!	1787.829	2.854981	8.418789	24.89878	0	31.3016	11.98541	10.69083	1.238973	5.758916		7.536963
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g		ug/g
total	#VALUE!	#VALUE!	#VALUE!	15460.59	4302.03	5143.132	4644.65	4383.236	2671.082	2954.057	2673.825	X	2365.48

Run 10 Report									
sample	R10-1	R10-2	R10-3	R10-4	R10-5	R10-6	R10-7	R10-8	R10 Rinse
temp	200	250	250	250	275	275	275	285	post run
time@T	0	0	2	2	1	2	2	1	glassware
A. Date	1/7/96	1/7/96	1/7/96	1/7/96	1/7/96	1/7/96	1/7/96	1/7/96	3/16/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	absolute
1cb	107.4949	84.01312	93.14192	81.02855	19.0016	11.32856	15.02757	13.71522	7.92173
2cb	1471.192	2031.687	26.28847	25.3576	1.735619	0	0	0	221.9103
3cb	341.0168	599.4667	0.755658	0.721278	0.128182	0	0	0	51.25736
4cb	1446.899	1623.08	0.943951	0.839371	0.259664	0.172125	0	0	131.5701
5cb	1880.306	279.886	0.397584	0.441329	0.052106	0	0	0	126.1444
6cb	7472.04	30.68311	0.534627	0.759249	0	0	0	0	325.2804
7cb	5716.943	8.940293	1.661465	1.602644	0.039912	0	0	0	218.4027
8cb	1093.96	63.69233	0.220832	0.19402	0	0	0	0	95.81742
9cb	181.49	244.1709	0	0	0	0	0	0	28.97543
10cb	29.23735	34.69222	0.059001	0	0	0	0	0	12.65641
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug
total	19740.58	5000.312	124.0035	110.944	21.21708	11.50068	15.02757	13.71522	1219.936
						4pk@1cb	4pk@1cb	4pk@1cb	
worksheet									

Run 11 Report						
sample	R11-1	R11-2	R11-3	R11-3 (5x)	R11-4	R11-4 (5x)
temp	bulk	250	300	300	350	350
time@T	feed	2	1.5	1.5	2	2
A. Date	NA	NA	1/24/96	1/24/96	1/24/96	1/24/96
type			soild samp	soild samp	soild samp	soild samp
1cb			7.173058	2.350501	0	3.211095
2cb			15.00764	16.0282	7.011903	27.39472
3cb			7.868972	8.549655	3.862763	6.345694
4cb			37.7104	50.73201	14.742	17.05277
5cb			90.79805	122.588	23.01152	24.77317
6cb			237.6581	305.8043	55.08408	60.70478
7cb			67.57617	89.95135	14.92232	14.61076
8cb			14.25523	27.65073	5.646226	6.725843
9cb			6.143779	10.59521	1.494324	1.978978
10cb			5.090475	7.483384	0.591382	0.913337
units			ug/g	ug/g	ug/g	ug/g
total	X	X	489.2819	641.7334	126.3665	163.7111
worksheet						

Run 12 Report

sample	R12 Feed	R12-1	R12-2	R12-3	R12-4	R12-5	R12-6	R12-7	R12-7A	R12-8	R12-8A	R12CB	R12B
temp	dry	220	field lw104	275	275	275	275	275	275	275	275	carbon	blank
time@T		0	blank	0	1	2	3	4	4	4	4	bed	solvent ext
A. Date	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96
type	soild samp	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	soild samp	oil clean
1cb	8.387705	115.5516	2.156608	174.6645	5.337356	5.641807	2.73488	5.713856	4.379356	3.245761	3.340907	17.01308	1.410584
2cb	475.6669	1074.398	0	460.6471	0	0	0	0	0	0	0	0	0
3cb	238.5279	188.1543	0	4.452641	0	0	0	0	0	0	0	0	0
4cb	299.252	172.2908	0	2.746831	0	0	0	0	0	0	0	0	0
5cb	224.5976	490.078	0	0.15498	0	0	0	0	0.065954	0	0	0.723218	0.451888
6cb	300.7272	6116.651	0.205166	0.078637	0	0	0	0	0	0	0	0	0
7cb	10988.6	13272.51	1.851067	3.26264	0.46668	0.942035	0.703736	0.576394	0.144029	0.573578	0.23779	2.291355	2.038178
8cb	54975.9	10325.55	0.404356	2.207634	0	0	0	0	0	0	0	0	0
9cb	35884.57	1851.986	0.147077	0	0	0	0	0	0	0	0	0	0
10cb	10485.48	528.2772	0	0	0	0	0	0	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	113881.7	34135.45	4.764275	648.215	5.804036	6.583842	3.438616	6.290249	4.589339	3.819339	3.578697	20.02765	3.900649
					4pk@1cb	4pk@1cb	4pk@1cb	4pk@1cb	4pk@1cb	4pk@1cb	4pk@1cb		4pk@1cb
worksheet													

Run 13 Report					
sample	R13-1	R13-2	R13-3	R13-4	R13-5
temp	MTR	MTR	final	solids frm	soilds frm
time@T	sample	drain	product	MTR	condensr
A. Date	NA	NA	3/16/96	NA	NA
type			soild samp		
1cb			87.9734		
2cb			1861.367		
3cb			1068.547		
4cb			4343.913		
5cb			12268.97		
6cb			38723.4		
7cb			11138.35		
8cb			1225.729		
9cb			216.9164		
10cb			0		
units			ug/g		
total	X	X	70935.16	X	X

Run 14 Report

sample	R14-1	R14-2	R14-3	R14-4	R14-5	R14-6	R14-7
temp	124	234	275	275	275	275	275
time@T	0	0	0	1	2	3	4
A. Date	3/16/96	NA	3/16/96	3/16/96	3/16/96	3/16/96	3/16/96
type	oil clean		oil clean	oil clean	oil clean	oil clean	oil clean
1cb	0		26.00725	95.38742	12.66799	6.51287	12.62451
2cb	225.6953		435.0351	112.2145	0.350106	0	0
3cb	93.02416		105.6018	1.337486	0	0	0
4cb	97.82317		#VALUE!	2.933295	0	0	0
5cb	76.79603		81.60498	1.647629	0	0	0
6cb	117.6247		#VALUE!	1.864091	0	0	0
7cb	4710.49		21.0267	2.622006	0.148503	0.255232	0.630317
8cb	#VALUE!		34.87839	0.765591	0	0	0
9cb	#VALUE!		70.66895	0	0	0.068522	0
10cb	4507.155		0	0	0	0	0
units	ug/g		ug/g	ug/g	ug/g	ug/g	ug/g
total	#VALUE!	X	#VALUE!	218.772	13.1666	6.836624	13.25483

Run 15 Report

sample	Paint Chip	Paint Chip	R15-1	R15-2	R15-3	R15-3	R15-4	R15-5	R15-6	R15-6	R15-7	R15-8	R15-9
temp	Feed (dry)	Feed (dry)	110	250	250	250	250	250	300	300	300	300	350
time@T	sup only	homgenizd	0	0	1	1	1	2	1	1	1	2.17	1
A. Date	4/2/96	4/2/96	4/2/96	4/2/96	4/2/96	6/7/96	4/2/96	4/2/96	4/2/96	6/7/96	4/2/96	4/2/96	4/2/96
type	soild samp	soild samp	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	9.956424	28.98059	4.068913	12.19326	12.70895	17.74153	18.17008	14.86387	9.513404	28.87053	10.37304	8.217676	4.550593
2cb	23.18886	46.92133	2.526336	5.024497	4.428602	4.579565	5.167353	5.564083	3.003347	3.550326	3.163818	3.339437	5.578474
3cb	4.793671	5.828698	0.381926	0.817375	0.293451	0.604681	0.31691	0.358158	0.450408	0.488614	0.316166	0.390372	1.074814
4cb	21.74133	24.39179	3.751255	4.317306	3.890268	3.378369	3.626024	4.140389	4.01904	3.876936	4.242048	4.612811	8.906646
5cb	83.10788	92.11301	6.788932	8.698009	8.359215	13.63899	7.993805	8.929265	8.958196	13.54326	9.014202	9.539202	13.47329
6cb	297.8192	319.3665	51.54247	71.35779	67.60449	79.09145	66.55509	75.94303	75.09406	76.18525	74.15396	76.10519	63.02702
7cb	77.43558	82.09418	19.30402	26.2187	26.83853	35.67989	25.11357	28.32017	27.16082	33.70136	26.62492	26.32818	13.20877
8cb	7.387288	7.872888	1.307677	1.807642	3.305338	2.548167	1.732277	2.01526	1.974772	2.204984	1.772211	1.614984	0.121106
9cb	0.762144	0.892324	0.138854	0.150937	2.112295	0.240727	0.149445	0.184666	0.212456	0.193572	0.154032	0.121835	0
10cb	0.163489	0.389329	0	0	0	0	0	0	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	526.3559	608.8506	89.81038	130.5855	129.5411	157.5034	128.8246	140.3189	130.3865	162.6148	129.8144	130.2697	109.9407

worksheet

sample	R15-9	R15-10	R15-10	R15-11	R15-12	R15-13	R15-14
temp	350	350	350	350	350	blank	solid
time@T	1	1	1	2	2	LW110	residual
A. Date	4/2/96	4/2/96	6/7/96	4/2/96	4/2/96	4/2/96	NA
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	
1cb	4.550593	6.123353	11.27473	7.512359	11.97446	4.119816	
2cb	5.578474	6.358256	8.245606	13.04919	13.91038	0	
3cb	1.074814	1.753248	1.990602	3.846223	4.081618	0	
4cb	8.906646	8.404618	8.200998	14.10508	14.20265	0	
5cb	13.47329	13.64012	18.86721	17.10041	19.86155	0	
6cb	63.02702	63.2624	63.90771	51.07973	43.14243	0	
7cb	13.20877	13.22125	15.72802	7.638234	5.317716	0.363066	
8cb	0.121106	0.163597	0.147819	0.208888	0	0	
9cb	0	0	0	0.069686	0	0.019441	
10cb	0	0	0	0	0	0	
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	
total	109.9407	112.9268	128.3627	114.6098	112.4908	4.502323	X

Run 16 Report								
								open head
sample	R16-1	R16-2	R16-3	R16-4	R16-5	R16-6	R16-7	R16-8
temp	121	252	275	275	275	275	275	275
time@T	0	0	0	1	2	3	4	4
A. Date	NA	4/2/96	4/2/96	4/2/96	4/2/96	4/2/96	NA	4/2/96
type		oil clean	oil clean	oil clean	oil clean	oil clean		oil clean
1cb		33.58769	37.31492	142.3926	171.5989	149.3984		118.738
2cb		304.5624	495.9049	956.8294	469.6649	188.3544		79.63818
3cb		64.74226	212.0468	12.83058	1.101889	0.439061		0.187309
4cb		282.0141	1386.991	9.490743	1.632478	0.996661		0.511306
5cb		1498.212	1062.03	0.783184	0.281019	0.334703		0
6cb		7018.962	277.2525	1.359441	0.779055	0.875801		0.360219
7cb		581.4226	26.97626	9.550653	6.477701	4.128165		2.58371
8cb		43.26372	37.73592	11.59952	2.516826	0.816214		0.157569
9cb		33.58068	127.8961	0.867365	0.166963	0.221543		0
10cb		0	0	0.130206	0.059651	0.087643		0.033758
units		ug/g	ug/g	ug/g	ug/g	ug/g		ug/g
total	X	9860.347	3664.149	1145.834	654.2794	345.6526	X	202.2101
worksheet								

Run 17 Report									
sample	R17-1	R17-2	R17-3	R17-4	R17-5	R17-6	R17-7	R17-8	R17-9
temp	120	300	300	300	300	350	350	condens.	final
time@T	0	0	1	1	2	1	2	from MTR	product
A. Date	4/29/96	4/29/96	NA	NA	4/29/96	NA	4/29/96	NA	4/29/96
									acid/perm
type	oil clean	soild samp			soild samp		soild samp		soild samp
1cb	12.02311	2.48419			2.679515		1.619436		3.841043
2cb	15.73754	9.376482			0.679543		0		0
3cb	2.641599	2.219699			0		0		0
4cb	14.19167	2.488222			0.01661		0		0
5cb	28.52729	0.376213			0		0		0
6cb	183.0808	0.016924			0.036957		0		0
7cb	69.21843	0.118184			0.485981		0		0.325849
8cb	4.612182	0.005403			1.2643		0.160483		0
9cb	0.307887	0.004152			0.781961		0.018676		0
10cb	0	0			0		0		0
units	ug/g	ug/g			ug/g		ug/g		ug/g
total	330.3405	17.08947	X	X	5.944867	X	1.798596	X	4.166892
							4pk@1cb		4pk@1cb
worksheet									

Run 18 Report									
sample	R18-1	R18-2	R18-3	R18-4	R18-5	R18-6	R18-7	R18-7	R18 Cond
temp	154	218	275	275	275	275	275	275	aqueous
time@T	0	0	0	1	2	3	4	4	ph. only e
A. Date	4/29/96	4/29/96	4/29/96	4/29/96	4/29/96	4/29/96	4/29/96	4/29/96	6/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	soild samp
1cb	49.67171	58.3586	103.9998	16.1208	2.215967	2.024227	3.287089	2.045092	1.153163
2cb	342.1996	505.1076	1590.149	2.591807	0	0	0.398653	0	0.251709
3cb	111.7102	204.9808	330.5313	0	0	0.194729	0	0	0.019011
4cb	118.7866	1203.422	363.2322	0.46075	0	0	0.057556	0.054242	0.019023
5cb	102.8949	2486.903	11.64501	0.125011	0	0	0.065206	0	0.023761
6cb	169.2691	7852.24	13.86416	0	0	0	0.409059	0	0.050455
7cb	4335.144	1597.258	17.3667	0.498053	0.275918	0.703094	0	0.362899	0.082687
8cb	19059.35	114.295	46.3479	0	0	0.18441	0	0.27794	0.017705
9cb	8444.14	69.97517	41.29852	0	0	0	0	0.135239	0.001531
10cb	3073.21	0	4.994752	0	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	35806.38	14092.54	2523.429	19.79642	2.491886	3.10646	4.217563	2.875412	1.619045
					4pk@1CB	4pk@1CB	4pk@1CB	4pk@1CB	
worksheet									

Run 19 Report

sample	R19-1	R19-2	R19-3	R19-4	R19-5	R19-6	R19-7
temp	0	0	0	1	2	3	4
time@T	138	217	275	275	275	275	275
A. Date	6/7/96	6/7/96	6/7/96	6/7/96	6/7/96	6/7/96	6/7/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	11.3813	9.319247	3.673331	8.564363	11.75622	20.17049	21.91239
2cb	15.53503	19.18593	28.30647	53.41306	69.44474	112.2544	136.7198
3cb	2.812499	1.962505	5.614223	12.06368	10.74715	20.40815	16.33413
4cb	14.60176	16.37781	35.21582	46.05749	38.75471	48.80237	38.21212
5cb	45.04688	69.83562	90.07662	66.13299	29.52068	29.85636	15.68219
6cb	223.2551	301.0691	193.9116	60.39972	15.15092	8.284644	2.475994
7cb	55.64807	42.91345	9.615585	1.305009	1.951776	0.423954	0.414491
8cb	5.675543	0.879266	0.114865	0.079501	0.228726	0	0
9cb	0.65341	0.070156	0.097306	0.064243	0.081859	0	0
10cb	0.113116	0	0	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	374.7227	461.6131	366.6258	248.0801	177.6368	240.2004	231.7511
worksheet							

Run 20 Report

sample	R20-1	R20-2	R20-3	R20-4A	R20-4B	R20-5	R20-6	R20-7	R20-8
temp	170	230	275	275	275	275	275	275	final
time@T	0	0	0	1	1	2	3	4	cond.
A. Date	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	NA	8/22/96
type	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean		oil clean
1cb	12.48626	5.8544	10.07826	37.01579	37.90996	40.73832	25.86113		51.38473
2cb	18.88866	16.372	71.52384	326.798	324.3716	286.5638	342.7922		326.6633
3cb	1.806073	4.923747	23.73568	45.67983	47.64513	23.77679	32.05726		25.27092
4cb	15.56019	25.47785	47.61779	45.89558	45.24675	21.02543	26.85324		20.21836
5cb	36.24678	48.43123	17.20887	2.143451	2.531188	0.485059	0.61686		0.409542
6cb	287.1759	101.0854	6.307238	0	0	0	0		0
7cb	105.9744	7.78179	0.108764	0.079834	0.036044	0.060835	0		0
8cb	5.79126	0	0	0	0	0	0		0
9cb	0.373979	0	0	0	0	0	0		0
10cb	0	0	0	0	0	0	0		0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g		ug/g
	ok	ok	ok	drag	drag	drag	drag		drag
total	484.3034	209.9265	176.5804	457.6125	457.7407	372.6503	428.1807	X	423.9469
	"drag" samples contained PCB, but were affected by some form of peak drag on the GC column								
	Values marked "drag" are for relative indication only, and may not reflect actual PCB concentration								

Run 21 Report

sample	R21-1	R21-2	R21-3	R21-4
temp	product	product	product	oil
time@T	control	bicarb.	proprietary	cond.
A. Date	8/22/96	8/22/96	8/22/96	8/22/96
type	soild samp	soild samp	soild samp	oil clean
1cb	0.064133	0.005877	1.118956	987.9538
2cb	0.009959	0.002999	0.003652	1259.86
3cb	0.001499	0.000366	0.000792	200.0141
4cb	0.006472	0.003443	0.000442	430.4998
5cb	0.00476	0.002636	0.003612	1395.02
6cb	0.022099	0.015416	0.008214	4373.396
7cb	0.006983	0.007118	0.005351	#VALUE!
8cb	0.00039	0	0.001982	#VALUE!
9cb	0.001753	0.001632	0.000371	#VALUE!
10cb	0	0	0	#VALUE!
units	ug/g	ug/g	ug/g	ug/g
			higher, drg	contam
total	0.118047	0.039486	1.143374	#VALUE!

Pilot Run 1 Report								
sample	PR1 Feed	PR1-1	PR1-2	PR1-3	PR1-4	PR1-5	PR1 FP2	PR1
temp	dry	119	231	275	275	275	275	Reciever
time@T	feed	0	0	0	1	2	4	Oil
A. Date	6/23/96	6/23/96	6/23/96	6/23/96	6/23/96	6/23/96	6/23/96	6/23/96
type	soild samp	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean
1cb	144.456	0	0	0	68.76313	86.36033	12.15244	62.38575
2cb	3652.366	958.4548	1106.103	1023.058	1757.012	2120.966	1272.14	315.9583
3cb	1277.691	337.2175	389.2695	556.0842	902.0192	1086.965	671.705	47.59988
4cb	2038.155	364.0979	669.7582	2297.228	3381.011	3677.039	1998.464	46.93651
5cb	12872.04	3501.334	3849.948	7408.831	5400.608	4322.126	1363.478	89.09412
6cb	125653.2	25911.47	27328.13	11722.37	4647.055	2690.684	984.3194	142.1862
7cb	131355.6	32363	12686.41	3444.834	96.94402	40.03094	624.506	28.1283
8cb	43956	9312.894	1290.844	320.6641	42.34545	45.65383	181.6499	1.477384
9cb	2023.474	559.2878	174.7539	689.8319	156.8856	170.9318	95.2815	0.043773
10cb	267.9094	67.89866	60.81657	126.6337	0	0	0	0
units	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	323240.9	73375.66	47556.04	27589.54	16452.64	14240.76	7203.697	733.8102
worksheet								

Pilot Run 2 Report									
sample	PR2-1	PR2-2	PR2-3	PR2-4	PR2-5	PR2-6	PR2-7	PR2-8	PR2-9
temp	98	275	275	275	275	275	oil	water	water
time@T	0	0	1	2	3	4	cond	cond.	offgas
A. Date	NA	7/8/96	6/23/96	6/23/96	NA	6/23/96	7/8/96	NA	7/8/96
type		oil clean	oil clean	oil clean		oil clean	oil clean		soild samp
1cb		56.28662	135.6767	134.6055		124.1135	74.23112		0
2cb		3786.662	4317.491	4709.852		4811.303	819.1		0.047525
3cb		1863.372	1982.254	2050.325		1978.39	197.4336		0.091793
4cb		4720.814	5665.561	5344.798		4337.975	198.45		0.33235
5cb		4839.648	3198.286	2153.727		1052.181	143.1051		0.331074
6cb		2416.029	740.8582	395.7813		132.0361	48.65923		0.183856
7cb		30.2062	28.63475	88.0186		72.94653	1.287963		0.032746
8cb		126.5423	166.4341	213.7027		211.4101	0		0.027585
9cb		342.5577	500.8178	401.3688		525.7818	0		0.058003
10cb		0	0	0		40.2054	0		0
units		ug/g	ug/g	ug/g		ug/g	ug/g		ug/g
total	X	18182.12	16736.01	15492.18	X	13286.34	1482.267	X	1.104931
worksheet									

sample	PR3-1	PR3-2	PR3-3	PR3-3	PR3-4	PR3-4	PR3-5	PR3-5	PR3-5	PR3-6	PR3-6	PR3-7	PR3-8	PR3-FB	PR3CS
temp	110	275	275	275	275	275	275	275	275	275	275	water	oil	Field	Cakd Solid
time@T	17	0	1	1	2	2	4	4	4	4	4	condensat	condensat	Blank 104	on rxtr wall
A. Date	NA	7/8/96	7/8/96	6/23/96	7/8/96	6/23/96	7/8/96	6/23/96	8/22/96	7/8/96	8/22/96	7/8/96	7/8/96	7/8/96	8/22/96
				quick		quick		quick							
type		oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	oil clean	soild samp	oil clean	oil clean	soild samp
1cb		205.5942	9.871348	11.11877	9.469437	3.663821	11.09037	25.64726	3.363257	12.07529	3.336657	0.134765	183.8353	6.238355	0
2cb		565.3637	2.249043	0	0	0	0	1.810191	0.438221	0	0.901542	0.616488	2206.298	0	0.877014
3cb		4.901751	1.068945	0	0.111426	0	0.609129	0	0.103397	0.137247	0.270146	0.147758	299.9344	0	0.927937
4cb		4.039523	2.530561	0	0.338924	0	1.067027	0.084374	1.199185	0.384592	1.512362	0.198976	124.5979	0	2.153588
5cb		1.918329	1.713396	0.055468	0.290166	0	0.538024	0	0.885453	0.138327	1.018002	0.119688	3.341229	0	0.822247
6cb		3.688542	0.192078	0.060987	0.04573	0.070252	0	0.134764	0	0.043845	0	0.038888	0.386973	0	0.583494
7cb		23.19898	0.448132	0.294157	0.423101	0.215329	0.504871	0.122162	0	0.519794	0.036245	0.015577	0.974989	0.632386	0.172135
8cb		20.57409	0	0.068454	0.031832	0	0.032237	0	0	0	0	0.005544	0.814508	0	0.177773
9cb		2.438403	0	0	0	0	0	0	0	0	0	0.000269	0.86676	0	0.217925
10cb		0.371538	0	0	0	0	0	0	0	0	0	0	0	0	0.147444
units		ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
total	X	832.089	18.0735	11.59784	10.71062	3.949402	13.84166	27.79876	5.989512	13.29909	7.074952	1.277954	2821.05	6.870741	6.079557
							4pk@1cb		4pk@1cb	4pk@1cb	4pk@1cb				
worksheet															

Pilot Run 4 Report										minimum	reasonabl
										estimate	estimate
sample	PR4-1	PR4-2	PR4-3	PR4-4	PR4-5	PR4-6	PR4-7	PR4-8	PR4-9	PR4-9	PR4-9
temp	155	275	275	275	300	330	carbon	reactor	oil phase	oil phase	oil phase
time@T	0	0	1	2	1	1	bed	solid prod.	cond.	cond.	cond.
A. Date		8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96	8/22/96
										est	est
type		oil clean	oil clean	oil clean	oil clean	oil clean	soild samp	soild samp	oil clean	oil clean	oil clean
1cb		12.55846	26.47984	90.60699	31.24829	9.227437	1.485901	6.474062	380.3818	380.3818	380.3818
2cb		106.4457	228.6916	532.8496	69.06973	0	0.681603	2.983288	2581.409	2581.409	2581.409
3cb		27.27581	60.57787	96.85149	1.107632	0	0.043537	0.037678	#VALUE!	283.3458	353.0276
4cb		64.6669	141.8161	150.8367	0.594271	0	0.033325	0.088858	#VALUE!	384.2012	608.344
5cb		94.71776	75.67614	16.38792	0	0	0.023562	0.047796	#VALUE!	416.9945	523.5576
6cb		297.1753	69.77204	1.343524	0.073696	0	0.032666	0.135058	#VALUE!	1000.283	1344.572
7cb		58.4855	5.318032	3.141176	0.522285	0	0.02231	0.105654	#VALUE!	507.0418	579.141
8cb		10.97549	12.50572	18.6588	0.34089	0	0.010007	0.078628	#VALUE!	104.7681	104.7681
9cb		8.085057	15.1595	26.18331	0.176435	0	0.001446	0.049537	#VALUE!	8.154521	8.154521
10cb		0	0	0	0	0	0.000644	0	#VALUE!	2.089002	2.089002
units		ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
				smeared		smeared	apprx val.			est	est
total	X	680.386	635.9969	936.8595	103.1332	9.227437	2.335001	10.00056	#VALUE!	5668.668	6485.445
				drag samp		slight drag	partial	definate			
worksheet				(contam)		in 1-CB	extraction	PCB's			