



BLASLAND & BOUCK ENGINEERS, P.C.

ENGINEERS & GEOSCIENTISTS

6723 Towpath Road, Box 66, Syracuse, New York 13214 (315) 446-9120
FAX: (315) 449-0017

April 24, 1992

Ms. Bonnie L. Eleder
Remedial Project Manager
USEPA, Region V
HSRW-6J
77 West Jackson Boulevard
Chicago, IL 60604

Re: Sheboygan River and Harbor Site -
Draft ASRI Report

File: 176.07 #2

Dear Bonnie:

Enclosed are five (5) copies of the BEST Solvent Extraction Bench-Scale Study Final Report. This submittal should be inserted into Volume 3 of the draft ASRI Report (Appendix F-8). An appropriate number of copies have also been forwarded to WDNR.

Should you have any questions concerning the enclosed, please feel free to contact us.

Very truly yours,

BLASLAND & BOUCK ENGINEERS, P.C.

Dawn S. Foster, P.E.
Associate

DSF/mtt
Enclosures

cc: Robin R. Schmidt, Wisconsin Department of Natural Resources (5 copies)
Tom Wentland, Wisconsin Department of Natural Resources (3 copies)
Dennis R. Dawson, Esq., Tecumseh Products Company (1 copy)
Mark A. Thimke, Esq., Foley & Lardner (1 copy)
William H. Bouck, P.E., Blasland & Bouck Engineers, P.C.
Robert K. Goldman, P.E., Blasland & Bouck Engineers, P.C.

ROUTING SLIP

Subject:

Date:

From: Tom Wentland, Southeast District

6/4/92

To:

Jim Schmidt, SED

John Kuhnz, U.S. EPA
(HSRW-6J)
77 West Jackson
Boulevard
Chicago, IL 60604-3590

Frank Schultz, SED

Binyoti, SED

Bill Haubold, U.S. EPA
(HSRW-6J)
77 West Jackson
Boulevard
Chicago, IL 60604-3590

Tom Aartila, SED

Sharon Shaver, SED

Russ Hart, U.S. EPA
(HSRW-6J)
77 West Jackson
Boulevard
Chicago, IL 60604-3590

Robin Schmidt, SW/3

Mark Giesfeldt, SW/3

Linda Meyer, LC/5

Patty Hanz, LC/5

Comments:

Copies of April Progress report for

Sheboygan 176.07 #2 ASR1

+ 887.02 #2 Removal Action

+ BEST SOLVENT EXTRACTION
REPORT

**B.E.S.T.[®] BENCH-SCALE TREATABILITY
FINAL TEST REPORT**

SHEBOYGAN RIVER AND HARBOR SITE

for

Blasland & Bouck Engineers

March, 1992

Prepared by
RESOURCES CONSERVATION COMPANY
3006 Northup Way
Bellevue, WA 98004-1407

**B.E.S.T.[®] BENCH-SCALE TREATABILITY
FINAL TEST REPORT**

Sheboygan River and Harbor Site

TABLE OF CONTENTS

	<u>Page No.</u>
I. INTRODUCTION.....	1
SUMMARY.....	1
RCC BACKGROUND.....	1
THE B.E.S.T. SOLVENT EXTRACTION PROCESS.....	2
EQUIPMENT DESCRIPTION.....	4
AIR EMISSIONS AND ABATEMENT.....	4
BENCH-SCALE TREATABILITY TEST DATA CORRELATION TO FULL-SCALE PERFORMANCE.....	8
II. BENCH-SCALE TREATABILITY TESTING.....	11
OBJECTIVES.....	11
BENCH-SCALE TREATABILITY TEST DOCUMENTATION.....	11
SAMPLE PREPARATION.....	12
FEED COMPOSITIONAL ANALYSIS.....	12
TRIETHYLAMINE COMPATIBILITY TEST.....	14
FEED pH ADJUSTMENT.....	14
SAMPLE EXTRACTION/PRODUCT SOLIDS.....	15
TOXICITY CHARACTERISTIC LEACHING PROCEDURE ANALYSIS ON PRODUCT SOLIDS.....	18
SOLVENT EVAPORATION/OIL STRIPPING.....	19
DECANTATION OF SOLVENT FROM WATER.....	20
PRODUCT WATER.....	20
III. MASS BALANCES.....	22
SOLIDS MASS BALANCE.....	22
OIL MASS BALANCE.....	23
WATER MASS BALANCE.....	24
PCB MASS BALANCE.....	25
SUMMARY OF MASS BALANCE CALCULATIONS.....	25
IV. ECONOMICS.....	26
V. CONCLUSIONS.....	27

TABLE OF CONTENTS

(cont'd.)

	<u>Page No.</u>
FIGURE 1	
B.E.S.T. PROCESS BLOCK DIAGRAM.....	3
FIGURE 2	
B.E.S.T. PROCESS FLOW SCHEMATIC.....	5
FIGURE 3	
EXTRACTOR/DRYER MATERIAL FLOW.....	6
(B.E.S.T. PROCESS STEPS BATTERY LIMITS OPERATIONS)	
FIGURE 4	
B.E.S.T. MODEL 615 SITE PLAN.....	7
FIGURE 5	
BENCH-SCALE TREATABILITY TEST DATA CORRELATION.....	9
(GENERAL REFINING SITE PCB CONCENTRATIONS IN RAW SLUDGE & PRODUCT FRACTIONS)	
FIGURE 6	
BENCH-SCALE TREATABILITY TEST DATA CORRELATION.....	10
(COMPARISON OF BENCH-SCALE TO FULL SCALE PHASE SEPARATION PERFORMANCE FOR GENERAL REFINING SITE SLUDGE)	

**B.E.S.T.[®] BENCH-SCALE TREATABILITY
FINAL TEST REPORT**

Blasland & Bouck Engineers
Sheboygan River and Harbor Site

I. INTRODUCTION

SUMMARY

A bench-scale treatability test of the B.E.S.T. solvent extraction process was conducted on a sediment sample containing polychlorinated biphenyls (PCBs) from the Sheboygan River and Harbor site. A summary of the bench-scale treatability test results follows:

BENCH-SCALE TREATABILITY TESTS RESULTS

<u>Feed PCB Content, mg/kg (dry basis)</u>	<u>Product Solids PCB Content, mg/kg (dry basis)</u>	<u>PCB Removal Efficiency, %</u>
170	0.7	99.6

As can be seen from the data above, the PCB residual of the treated solids (Product Solids) was 0.7 mg/kg, yielding a PCB removal efficiency of 99.6%. In addition, the treated solids readily passed the TCLP Toxicity Test for the leaching of metals.

RESOURCES CONSERVATION COMPANY (RCC) BACKGROUND

Resources Conservation Company (RCC), established in 1971, is a multi-discipline engineering service that specializes in the design of hazardous waste and wastewater treatment systems. RCC is a wholly owned subsidiary of the Halliburton Company whose headquarters are in Dallas, Texas. RCC's main office is located in Bellevue, Washington. RCC's treatability laboratory is located near the main office. RCC has a staff of over 85 personnel.

THE B.E.S.T. SOLVENT EXTRACTION PROCESS

The B.E.S.T. process is a patented solvent extraction technology using triethylamine as the solvent. Triethylamine is an aliphatic amine that is produced by reacting ethyl alcohol and ammonia.

Triethylamine is an excellent solvent for treating hazardous wastes because it exhibits several characteristics that enhance its use in the solvent extraction system. These characteristics include:

- A high vapor pressure; therefore, the solvent can be easily recovered from the extract solution (oil, water, and solvent) via steam stripping.
- Formation of a low boiling temperature azeotrope with water, allowing the solvent to be recovered from the oil to very low residual levels (typically less than 100 ppm).
- A low heat of vaporization (1/7 of water), allowing solvent to be recovered from the treated solids with very low energy input.
- Triethylamine is alkaline (pH=10); therefore, some heavy metals are converted to the hydroxide form, precipitate and exit the system with the treated solids.
- Triethylamine readily biodegrades. Data available in EPA document EPA Data ORD USEPA Washington, D.C. 20460, Feb. 1983 (reprint) Manual, Volume 1 600/2-82-001a, shows that a level of 200 ppm triethylamine in water was degraded completely within 11 hours by the common soil bacteria *aerobacter*.

A block diagram of the B.E.S.T. process is presented in Figure 1. The first extraction of the feed is conducted at low temperatures (about 40 degrees F). At this temperature, triethylamine is soluble with water. Therefore, the extract solution contains most of the water in the feed sample. If the first extract solution contains sufficient water to allow a phase separation of the solvent and water, the extract is heated to a temperature above the miscibility limit (130 degrees F). At this temperature, the extract solution separates into two distinct phases, a solvent/oil phase and a water phase. The two phases are separated by gravity and decanted. The extract solution from subsequent stages is combined with the decanted solvent/oil phase from the first extraction stage. The solvent is recovered by steam stripping and evaporation.

Triethylamine is removed from the treated solids by indirect steam heating. A small amount of steam may be added directly to the dryer vessel to provide the water required to form the low boiling temperature azeotrope. Residual solvent remaining in the treated solids biodegrades readily, allowing the treated solids to be used as backfill at the site in some cases.

The B.E.S.T. process operates near ambient pressure and temperature and at an alkaline pH. Temperatures of the liquid streams within the the unit vary from about 40 to 170 degrees F, and elevated pressures are not required. This gives the B.E.S.T. process the advantage that it can use standard off-the-shelf processing equipment.

B.E.S.T. PROCESS CONCEPT

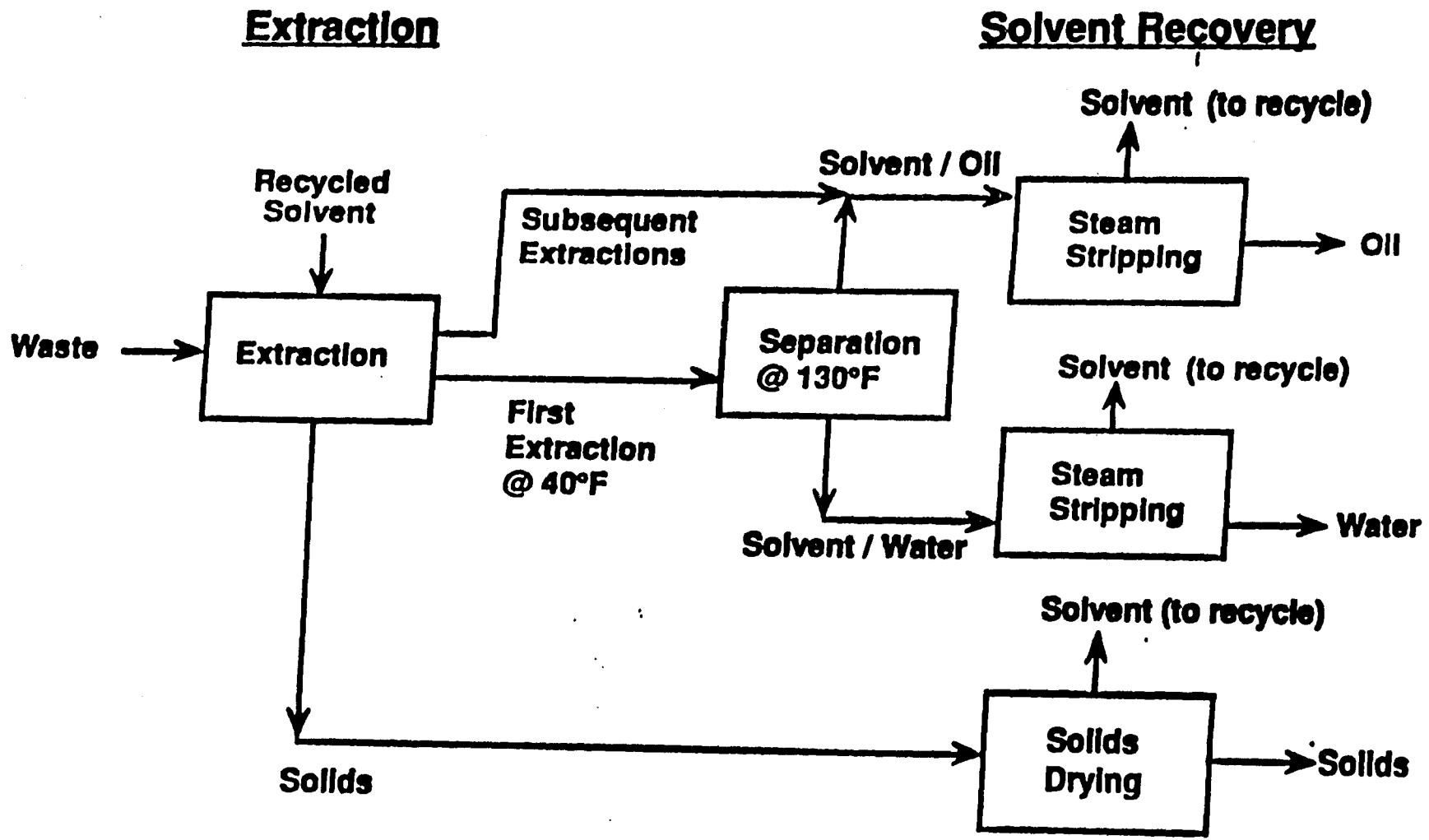


Figure 1

EQUIPMENT DESCRIPTION

RCC proposes using a B.E.S.T. Model 615 unit to treat the PCB-containing material at this site. The B.E.S.T. Model 615 unit has a design capacity of approximately 200-300 tons of feed per day. A flow schematic for the B.E.S.T. Model 615 is presented in Figure 2.

The B.E.S.T. Model 615 uses an extractor/dryer vessel to extract and dry the PCB-containing materials. The extractor/dryer is a horizontal, steam-jacketed vessel that allows for solvent contacting, mixing, solids/solvent separation, solids drying, and solids conditioning in one vessel. The extractor/dryer vessel is an off-the-shelf assembly that has a long history of reliable performance in a wide range of process industry applications.

PCB-containing materials are excavated from the site and screened to one inch maximum dimension. The screened material is then loaded into top-loading, bottom discharge hoppers. An overhead crane facilitates the positioning and lowering of the loaded hopper onto the loading port of the extractor/dryer unit. The flow of material through the extractor/dryer system is shown in Figure 3. Treated solids are discharged into hoppers and transported to a holding area.

Figure 4 provides the standard Site Plan for RCC's B.E.S.T. Model 615.

AIR EMISSIONS AND ABATEMENT

The B.E.S.T. process uses one vent to the atmosphere. The vent provides pressure equalization for the nitrogen blanketing system and a purge for noncondensable gases from process condensers. RCC uses a refrigerated condenser and an auxiliary water scrubber system to reduce solvent emissions from the vent.

During a performance test in February 1987 at the General Refining Superfund Site cleanup, a third party reported the following emissions from the B.E.S.T. process vent at a time when the auxiliary water scrubber was not in operation:

	<u>Emission Rate, lb/hr</u>
Benzene	0.00114
Mercury	< 0.000000043
Toluene	0.000614
Triethylamine	0.0954
Xylene	0.000884

RCC expects air emissions from future operations to be lower than these results. The use of the auxiliary water scrubber will lower the triethylamine release rate even further. RCC now utilizes activated carbon filters on the single vent line to achieve zero emissions of triethylamine.

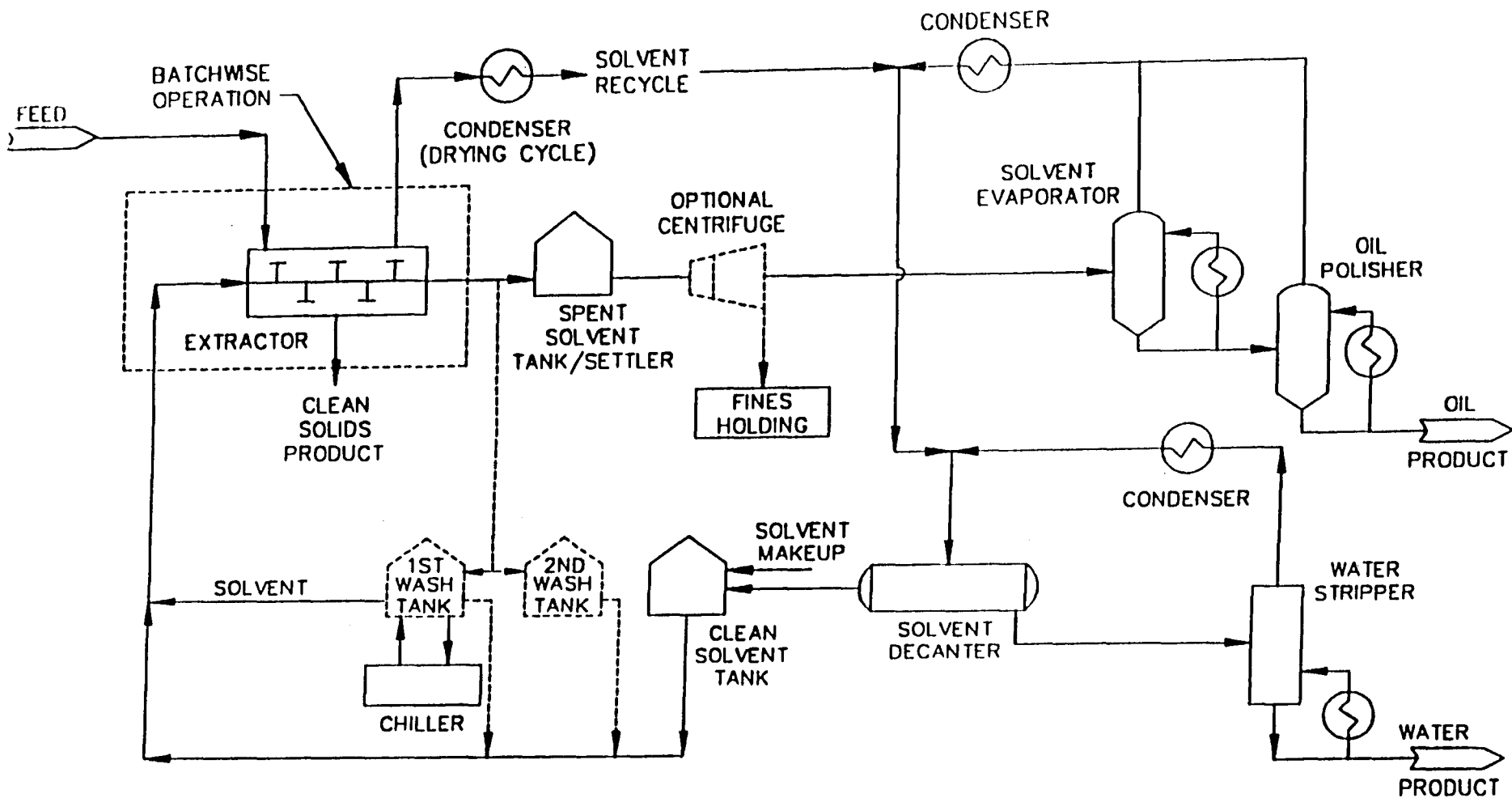


Figure 2

RCC Resources Conservation Company

ENG RECORD
DRAWN J. STANDIFORD
CHECKED
CHECKED
PROJ ENGR
APPROVED

PROCESS FLOW SCHEMATIC

B.E.S.T.[®] MODEL 315/615

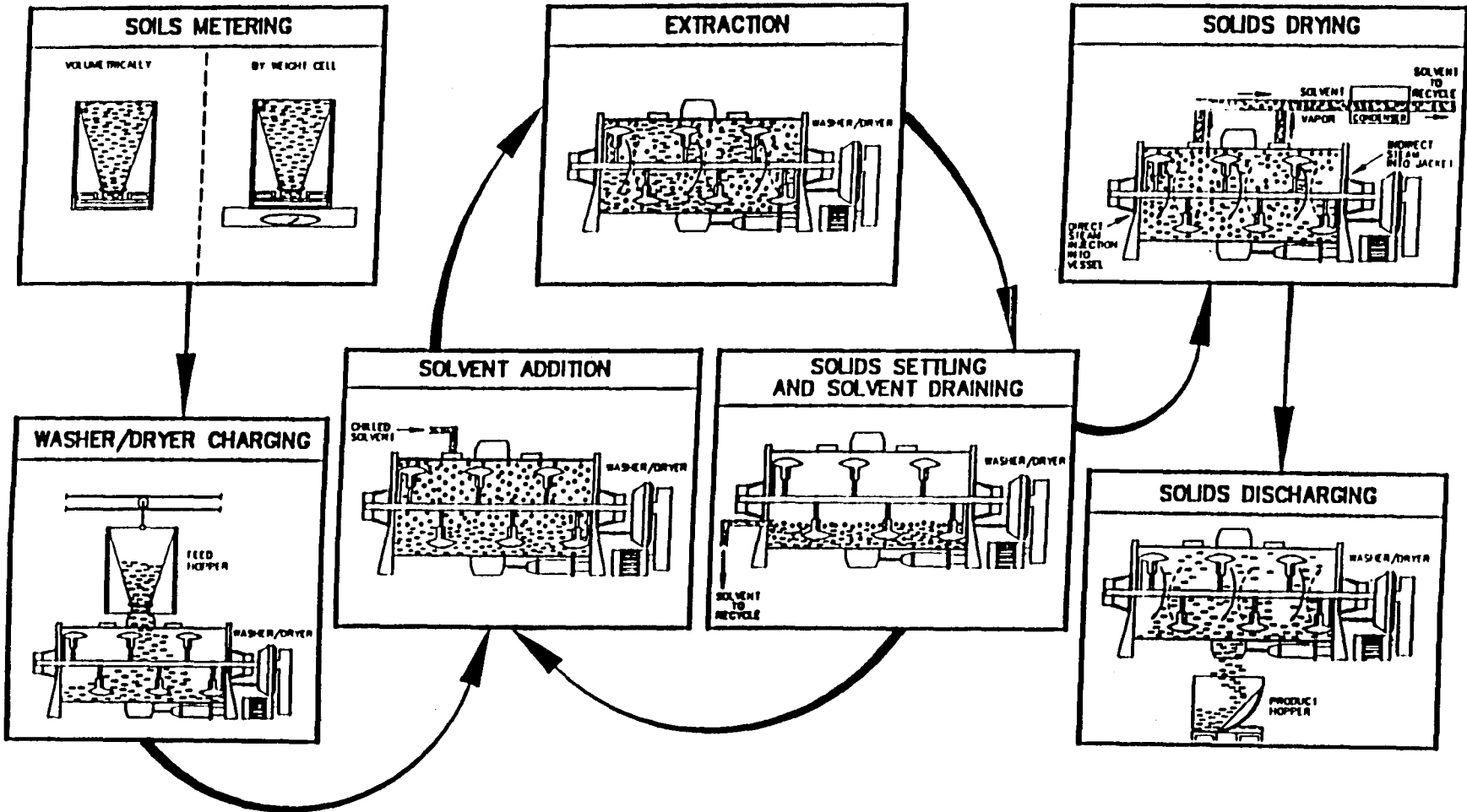
SOILS TREATMENT UNIT

DWG NO.
B-221

SHEET NO.
1 OF 1

REV

B.E.S.T.[®] PROCESS STEPS BATTERY LIMITS OPERATION



BENCH-SCALE TREATABILITY TEST DATA CORRELATION TO FULL-SCALE PERFORMANCE

In order to evaluate each potential application for the B.E.S.T. process, RCC has developed a low cost bench-scale treatability test protocol that provides data that closely simulates full-scale system performance. The bench-scale treatability test data allows RCC to evaluate the feasibility of the process on a particular sample and to estimate treatment costs.

The reliability of the bench-scale treatability tests to predict full-scale performance has been verified by the US EPA report Evaluation of the B.E.S.T. Solvent Extraction Sludge Treatment Technology - Twenty-Four Hour Test, by Enviresponse, Inc., under EPA Contract 68-03-3255. A quote from this report evaluating the B.E.S.T. process states:

"Resources Conservation Company has conducted many laboratory tests and developed correlations to which data from full-scale operations, such as the General Refining site, can be compared."

Figures 5 and 6 present data from two separate bench-scale treatability tests and full-scale operating performance data at the General Refining, Inc., Superfund site, as collected by an EPA contractor. This data demonstrates a close correlation between bench-scale treatability test data and full-scale operating data.

Bench-scale treatability testing provides valuable information about the use of the B.E.S.T. process at full-scale including:

- The PCB removal efficiency from the sample.
- Solids separation requirements for full-scale operation.
- The separation efficiency of water from the water/solvent/oil solution by decantation.
- General information on the partitioning of metals and organic compounds in the oil, water, and solids products.
- Full-scale operating parameters to develop treatment costs.



GENERAL REFINING SITE
PCB CONCENTRATIONS IN RAW SLUDGE & PRODUCT FRACTIONS
(ppm)

	LAB SCALE TESTING (1986)		FULL SCALE PROCESSING
	TEST "A"	TEST "B"	FEB. 26-27, 1987
RAW SLUDGE (DRY BASIS) mg/kg	14.	12.	13.5
PRODUCT SOLIDS mg/kg *	0.02	0.14	<0.13
PRODUCT WATER mg/L	<0.01	<0.01	<0.005
%EXTRACTION EFFICIENCY	99.9	98.8	>99.0

* Dry Basis

Page 9

Figure 5

COMPARISON OF BENCH SCALE TO FULL SCALE
PHASE SEPARATION PERFORMANCE
FOR
GENERAL REFINING SITE SLUDGE

	Raw Sludge	Bench Scale			Raw Sludge	Full Scale		
		Separated Phase Fractions				Separated Phase Fractions		
		<u>Oil</u>	<u>Water</u>	<u>Solids</u>		<u>Oil</u>	<u>Water</u>	<u>Solids</u>
Oil %	36	>97.	.017	5.7	27	99.	0.0033	0.81
Water %	56	*	N/A	<1.0	66	0.88	>99.	<0.5
Solids %	8	*	N/A	>94.	7	*	0.81	>98.

N/A Not Available
* BS&W = 2.8%

Figure 6

II. BENCH-SCALE TREATABILITY TESTING

OBJECTIVES

Resources Conservation Company (RCC) has conducted a bench-scale treatability test on the Sheboygan River PCB-containing sediment sample. The primary objective of this test was to determine the feasibility and cost effectiveness of the B.E.S.T. solvent extraction process for treating the raw sediment, specifically:

- Determine effectiveness of the B.E.S.T. process for treating PCB-containing sediments from the site, including the PCB removal efficiency.
- Determine materials handling and other equipment needs for each sediment tested.
- Develop data to project process operating conditions for full-scale treatment, as well as estimate full-scale treatment costs.

BENCH-SCALE TREATABILITY TEST DOCUMENTATION

The documentation of the testing can be separated into three distinct categories. The following summarizes the procedures used for each step of the treatability process:

1. When the sample was received in the laboratory, the shipment was checked for correctness of accompanying paper work, including Chain of Custody. The information was recorded both in a hardbound sample logbook and on a computer system that has been specifically designed by RCC for use in tracking samples. The sample was issued a discrete laboratory sample number, and a test request form was completed. The sample was kept in a refrigerator under controlled and documented temperature prior to any lab analysis or the treatability study. Chain of Custody records and other information received with the sample are kept as part of the project file.
2. All records and observations taken during the bench-scale treatability testing were recorded in laboratory notebooks. The laboratory notebooks are the property of RCC, and each analyst and engineer has been issued a notebook. The notebooks are retained by RCC as permanent record of raw data collection.
3. Samples that were collected during the bench-scale test, including samples internal to the process, were submitted to the RCC analytical chemistry laboratory for further analysis. Each sample collected was issued a discrete laboratory number. An analysis request form was completed. The samples were analyzed in accordance with RCC's Laboratory Quality Management Plan and reviewed for correctness prior to issuance. A file is maintained to permanently store the accumulated test results from completion of the analytical testing.

SAMPLE PREPARATION

The PCB-containing sample from the Sheboygan River and Harbor Site arrived at RCC's laboratory in December, 1991. The sample was labeled BS-2. The sample was a wet, gray-colored mud with very little debris present, and had a strong sulfur odor.

The feed was screened using standard Tyler sieves to remove debris and to homogenize the sample. Very little debris was removed. Results of the screen analysis were as follows:

Sample Screening

<u>< 1/4 inch</u>	<u>> 1 inch</u>
> 97 %	none

Bench-scale testing requires material greater than 1/4 inch be removed. Full-scale processing requires that the feeds be screened to remove only material greater than 1 inch in diameter.

FEED COMPOSITIONAL ANALYSIS

The feed was analyzed for percent oil, water, solids, PCBs, and metals per the following methods:

- The oil & grease content was determined as per Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 503D, with two exceptions: the extraction time was extended from 4 to 16 hours, and methylene chloride (MeCl_2) was substituted for Freon based on RCC experience that MeCl_2 is a better solvent for oils and greases.
- The water content was determined by weight loss at 105 degrees C.
- The PCB concentration was determined per EPA Publication SW846 Test Methods for Evaluating Solid Waste, Method 8080. The sample extraction method was by Soxhlet extraction with 1:1 acetone:hexane for 16 hours. The PCBs were quantitated as Aroclor 1242.
- The metals composition (except for Mercury) was determined by nitric acid digestion after ashing at 550 degrees C, followed by ICP analysis (EPA SW846, Method 6010).
- Mercury concentration was determined by the Cold Vapor Technique, Method 303F, of Standard Methods for the Examination of Water and Wastewater.
- Loss-on-ignition was determined by heating a sample from 105 to 550 degrees C which is a measure of the total organic content.
- Bulk density was determined by weighing a specific volume of sample.

The results of these analyses on a wet basis were as follows:

Feed Compositional Analysis

(wet basis unless noted)

<u>Analyte</u>	<u>Result</u>
Oil & Grease (by MeCl ₂), %	0.55
Water, %	40.
Solids, %	59.
Loss-on-ignition, % (dry basis)	6.6
PCBs, mg/kg, dry basis	170.

The heavy metals composition of each feed was as follows:

Feed Metals Composition, mg/kg

(As received basis)

<u>Analyte</u>	<u>Result</u>
Arsenic	< 50.
Barium	47.
Cadmium	< 5.
Chromium	25.
Copper	14.
Lead	32.
Mercury	0.38
Nickel	9.
Selenium	< 50.
Silver	< 5.
Zinc	85.

TRIETHYLAMINE COMPATIBILITY TEST

Triethylamine is a compound with a unique chemical structure. The geometry of the structure is tetrahedral, meaning that the nitrogen atom is at the center of a three-sided pyramid. The four points of the pyramid structure are occupied by three ethyl functional groups and one electron cloud. This structure gives triethylamine dual polarity characteristics. The ethyl groups are essentially nonpolar; the electron cloud is polar. Although triethylamine is a very stable solvent, there is a remote possibility that the electron pair can react with certain types of materials. In order to determine if this will occur with a sample, a compatibility test is performed. This involves mixing of the sample with triethylamine and making observations as to the heat of solution and any other visual signs of reaction.

When each feed sample was mixed with cold triethylamine, there were no visible signs of adverse reactions and the heat of solution was in a normal range. The triethylamine was observed to darken upon mixing, indicating that extraction of the organic compounds was occurring.

Based on the favorable results of this preliminary test, it was decided that the B.E.S.T. bench-scale treatability test should proceed.

FEED pH ADJUSTMENT

Triethylamine can be ionized at low pH to triethylammonium salts that cannot be removed from the products. The alkaline nature of triethylamine will buffer the pH of the sample to a pH of around 9. The solvent spent in the pH buffering will be lost. In order to efficiently recover the triethylamine from the separated phase fraction products, the pH of the sample is adjusted to about 11 with caustic soda.

A 5-gram portion of each feed sample was slurried with deionized water. The pH of this mixture indicated that caustic would need to be added to each sample. Incremental portions of caustic soda (NaOH) were added to bring the pH to 11. The amount of caustic that was required to perform this pH adjustment and the original sample pH is summarized below:

Sample pH and Caustic Dose

<u>pH</u>	<u>Caustic Dose</u> <u>(mls 50% NaOH per kg)</u>
8.0	5.1

SAMPLE EXTRACTION/PRODUCT SOLIDS

A portion of sediment was prechilled by placing it in a 4-liter resin kettle, immersed in a temperature controlled water bath set at 0.5 degrees C. The sediment pH was adjusted by adding caustic soda at the same time that chilled triethylamine was added. Mixing was performed by an air-driven propeller mixer. As expected, the solvent became colored, indicating extraction of organic compounds was occurring. The mixing was stopped and settling characteristics were observed. The liquid in the mixture was decanted off and then separated from any remaining solids by centrifuging at 2100 rpm for 10 minutes. The solvent/oil/water mixture was temporarily set aside after centrifugation for testing as discussed later under solvent evaporation/oil stripping.

No additional caustic was added for the additional extraction stages. The decanted TEA/Oil from the subsequent extraction stages was not centrifuged. The improved settling characteristics observed during the subsequent extractions resulted in a TEA/Oil mixture which was free of suspended solids. A total of six extraction stages were conducted on the material. Solids samples were collected from each extraction stage. The final extraction solids are hereafter referred to as Product Solids.

Product Solids were analyzed per the following methods. Additionally, 4th, 5th and 6th extraction stage solids were analyzed for PCBs to allow a determination of when the point of diminishing returns with respect to PCB reduction is achieved.

- The oil & grease content was determined as per Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 503D, with two exceptions: the extraction time was extended from 4 to 16 hours, and methylene chloride (MeCl_2) was substituted for Freon based on RCC experience that MeCl_2 is a better solvent for oils and greases. The O & G content was also determined using the Freon protocol.
- Loss-on-ignition was determined by heating a sample to 550 degrees C for 3 hours.
- The PCB concentration was determined per EPA Publication SW846 Test Methods for Evaluating Solid Waste, Method 8080. The sample extraction method was by Soxhlet extraction with 1:1 Acetone:Hexane for 16 hours. The PCBs were quantitated as Aroclor 1242.
- The metals composition was determined by aqua regia digestion, followed by ICP analysis (EPA SW846, Method 6010).

- Mercury concentration was determined by the Cold Vapor Technique, Method 303F, of Standard Methods for the Examination of Waste and Wastewater.
- The triethylamine content was determined by shaker bath water extraction and packed column gas chromatography with a flame ionization detector.
- The pH was determined by measuring the pH of a slurry of 5 grams of sample and 50 mls of deionized water. The slurry was tested by pH probe after mixing.

PCB analytical results of all of the solids samples were as follows:

PCB Analysis Summary, mg/kg
(all data dry basis)

<u>Sample Point</u>	<u>Result</u>
Feed	170.
4th Stage Solids	1.9
5th Stage Solids	1.1
Product Solids (6th Stage Solids)	0.73

Additional product solids analyses, all on a dry basis since the product solids were dried in-process, follows:

Product Solids Analysis
(six extraction stages)

<u>Analyte</u>	<u>Result</u>
Oil & Grease (by MeCl ₂), %	< 0.2
Triethylamine, mg/kg	< 15.
Loss-on-ignition, %	6.3

PCB removal efficiency is determined by comparing the amount of PCBs in the feed to the amount remaining in the sediment after treatment. The fraction of PCBs remaining in the sediment is calculated by dividing the PCB content of the product solids by the PCB content of the feed, on a dry basis. The calculation of the Sheboygan River sample follows:

PCB Removal Efficiency Calculation

.....

$$\begin{aligned} \text{Fraction of PCBs remaining in sediment} &= \frac{\text{Product solids PCB Content (dry basis)}}{\text{Feed PCB Content (dry basis)}} \\ &= \frac{0.73 \text{ mg/kg}}{170 \text{ mg/kg}} = 0.00429 \end{aligned}$$

.....

$$\begin{aligned} \% \text{ Removal from sediment} &= 100 \cdot (1 - \text{fraction of PCBs remaining in sediment}) \\ &= 100 \cdot (1 - 0.00429) \\ &= 99.6 \% \end{aligned}$$

The reduction in the PCB content and the corresponding removal efficiency of PCBs from the sediment is summarized below.

Total PCB Removal Summary

<u>PCBs in Feed, mg/kg</u> (dry basis)	<u>PCBs in Product Solids, mg/kg</u> (dry basis)	<u>Removal Efficiency, %</u>
170.	0.73	99.6

Total heavy metal analysis of the product solids was as follows:

Product Solids
Total Metals Analysis, (mg/kg)
(Dry Basis)

<u>Analyte</u>	<u>Result</u>
Arsenic	< 50.
Barium	77.
Cadmium	< 5.
Chromium	44.
Copper	31.
Lead	50.
Mercury	0.29
Nickel	12.
Selenium	< 50.
Silver	< 5.
Zinc	130.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE ANALYSIS ON PRODUCT SOLIDS

The product solids from each sample were extracted using the Toxicity Characteristic Leaching Procedure (TCLP) in accordance with Federal Register, March 29, 1990. Each TCLP leachate was analyzed for metals content. The results from this analysis were as follows:

Product Solids
TCLP Leachate Analysis, mg/l

<u>Analyte</u>	<u>Result</u>	<u>Regulatory Level, mg/l</u>
Arsenic	< 0.5	5
Barium	0.64	100
Cadmium	< 0.05	1
Chromium	< 0.05	5
Lead	< 0.3	5
Mercury	0.002	0.2
Selenium	< 0.5	1
Silver	< 0.05	5

As can be seen from the above data, all Product solids readily passed the TCLP test for metals.

SOLVENT EVAPORATION/OIL STRIPPING

Recovery of product oil (the organic compound in the feed) was accomplished by distilling off the triethylamine. This was done by boiling the triethylamine/oil/water extract in a Buchi Rotovapor[®] apparatus. The oil remained in the boiling flask of the Rotovapor while the triethylamine was condensed as it evaporated and was collected separately. A small amount of triethylamine was deliberately left in the oil because of the extremely low oil content in the feed samples. In this fashion, the oil could be transferred from the Rotovapor flask and the oil would still be homogenous which is very important for the integrity of the PCB mass balance. (The PCB mass balance is discussed on page 25.) Normally the oil is further treated to remove residual solvent.

The analysis of each product oil was performed as follows:

- The solids content is calculated by ashing at 550 degrees C. The fraction of ash to "oil" is considered the "solids" content.
- The PCB concentration was determined by dilution of the oil in hexane, followed by EPA SW846 (Test Methods for Evaluating Solid Waste), Method 3620, Florisil column cleanup and/or sulfuric acid digest. Then the prepared sample was analyzed by EPA SW846, Method 8080.
- The metals composition was determined by nitric acid digestion after ashing at 550 degrees C, followed by ICP analysis (EPA SW846, Method 6010).

The product analysis results reported after the triethylamine remaining in the oil is factored out were as follows:

Product Oil Analysis

<u>Analyte</u>	<u>Result, Oil Basis</u> (triethylamine-free)
PCBs, mg/kg	40,000.
Solids, %	0.2
Metals, mg/kg	
Arsenic	< 210
Barium	16.
Cadmium	< 21.
Chromium	< 21.
Copper	110.
Lead	145.
Nickel	35.
Selenium	< 210
Silver	< 21.
Zinc	19.

The Product Oil was not analyzed for triethylamine and water since the Product Oil was left in solution with triethylamine due to the low oil content of the feed. This makes an analysis of "triethylamine residual" meaningless. Analysis of "water residual" is also meaningless since water is normally removed with the solvent.

The distilled and condensed solvent also carries water in the form of an azeotrope. The solvent/water mixture was further processed as per the next section, DECANTATION OF SOLVENT FROM WATER.

DECANTATION OF SOLVENT FROM WATER

The solvent recovered from each extraction stage was separated into its aqueous (water), oil and solvent components. Only the extract from the first extraction stage had a significant amount of water in solution, so only the water in the first stage extract is recovered.

The water was separated from the extract by evaporation. When the triethylamine/oil/water first stage extract was evaporated, as described in section SOLVENT EVAPORATION/OIL STRIPPING, the water formed an azeotrope with the distilled triethylamine, leaving the oil behind. The water was then separated from the triethylamine of the condensed triethylamine/water azeotrope by decantation. The triethylamine/water recovered from the Solvent Evaporation/Oil Stripping step was heated to 140 degrees F, then poured into a 4-liter separatory funnel. Separation occurred immediately, therefore, a temperature control system was not required. As expected, this separation was highly effective because virtually no oil or solids in the condensed triethylamine/water could hinder the separation of triethylamine from water by decantation.

PRODUCT WATER

Removal of residual triethylamine from each decant water was accomplished by heating the water on a hot plate while maintaining an elevated pH. The elevated pH is necessary to ensure that the majority of the triethylamine remains in the volatile molecular form. Triethylamine/water azeotrope boils at about 170 degrees F. When the triethylamine is removed, the water temperature increases to 212 degrees F. Analysis of each stripped water, labeled Product Water, was conducted as follows:

- The total solids content was per EPA Methods for Chemical Analysis of Water and Wastes, Method 160.3
- The triethylamine content was determined by packed column gas chromatography with a flame ionization detector.
- The metals content was determined by nitric acid digestion followed by ICP analysis (EPA SW846, Method 6010).
- There was insufficient sample for Oil & Grease or PCB analyses.

Results of these analyses were as follows:

Product Water Analysis, mg/l

<u>Analyte</u>	<u>Result</u>
Total Solids	1000.
Triethylamine	7.
pH	10.7

The bulk of the total solids content is attributed to sodium due to the addition of sodium hydroxide.

Product Water
Total Metals Analysis, mg/l

<u>Analyte</u>	<u>Result</u>
Arsenic	< 0.5
Barium	0.06
Cadmium	<0.05
Chromium	< 0.05
Copper	< 0.05
Lead	< 0.3
Nickel	< 0.05
Selenium	< 0.5
Silver	< 0.05
Zinc	0.13

III. MASS BALANCES

The data gathered during the bench-scale treatability test provides the data required to calculate mass balances. The mass balances have been segregated into four groups: solids, oil, water, and PCBs.

SOLIDS MASS BALANCE

The mass balance for solids is a comparison of the solids input during the test to the solids recovered after the test. The mass of solids input during the test includes the solids portion of the feed extracted and the solids portion of caustic soda added. The solids portion of the feed extracted was calculated by multiplying the weight of feed extracted by the solids content as determined by analysis. The solids portion of the caustic soda added was calculated by multiplying the weight of the 50 percent NaOH solution added by 0.50.

The mass of the solids recovered from the test is equivalent to the sum of the product solids and samples taken for stage-by-stage assays. A summary of this data follows:

Solids Mass Balance

Total Feed Extracted, Wet Basis	1500 g
Solids Portion of Feed	870 g
Solids Portion of Caustic	+ 5.4 g
	<hr/>
Total Calculated Solids Input	= 875 g

.....

Weight of Product Solids Recovered	759 g
Weight of Solids Samples Recovered	+ 123 g
	<hr/>
Total Solids Recovered	= 882 g

.....

Recovery, %	101
-------------	-----

OIL MASS BALANCE

The oil mass balance was computed by the same method used in calculating the solids mass balance. The oil & grease content of each feed was determined by extracting a sample of the feed with methylene chloride. This oil & grease content (by MeCl_2) was multiplied by the weight of the feed input to determine the amount of oil input. The mass of oil recovered from the test was equivalent to the product oil recovered. The residual oil in the product solids and product water was negligible when calculating an oil mass balance.

The oil mass balances (based on methylene chloride) were as follows:

Oil Mass Balance

<u>Calculated Oil Input</u>	<u>Equivalent Product Oil Recovered</u>	<u>% Recovery</u>
8.3 g	5.2 g	63 %

Removal of the oil was good as evidenced by the low (< 0.2%) oil content of the Product Solids. However, the mass balance is lower than usual. This is attributed to analytical error in the determination of the oil content of the feed and/or the oil in triethylamine. The amount of oil recovered was low due to the low feed oil content and, therefore, the recovered oil was left in a triethylamine solution. As the feed oil content decreases, analytical error becomes more pronounced.

Virtually all of the PCBs from the sample now reside in the product oil. The weight of PCB-containing material was reduced from 1500 grams to 5.2 grams corresponding to a 300-fold reduction in mass.

WATER MASS BALANCE

The water mass balance was computed similarly to the method used for solids. The mass of water input came from the water in the feed, plus the water introduced with the caustic. The water portion of each feed was calculated by multiplying the weight of the feed by the water content as determined by analysis. The water portion of the caustic input was calculated by multiplying the weight of the 50 percent NaOH solution by half.

The mass of water recovered was equivalent to the sum of the decant water, residual water in the decant triethylamine/oil, and residual water in the subsequent extraction extracts. A summary of this data follows:

Water Mass Balance

Water Portion of Feed	615 g
Water Portion of Caustic	+ 5.5 g
	<hr/>
Total calculated water input	= 620 g

.....

Water recovered from decant water	430 g
	<hr/>
Total water recovered	= 430 g

.....

% Recovery	69
------------	----

The recovery of water was low. The temperature tends to increase above the triethylamine/water miscibility limit when the treated solids are centrifuged. At these conditions, some water may have exited the centrifuge with the solids. This water was lost when the solids were dried and cannot be quantified. In addition, a portion of the water in the feed was left behind in the resin kettle after decantation of the first extraction since it is not possible to decant all the solvent from the solids. This water was lost when the solids were dried. This portion of the water lost in the dryer is not accounted for in the water mass balance. (In RCC's Pilot Unit, and Full-Scale Unit, all such water is recovered from the dryer.)

PCB MASS BALANCE

The PCB mass balance was computed similarly to the method used for oil. The mass of PCBs input was calculated by multiplying the weight of each feed by the PCB concentration as determined by analysis. The PCBs recovered from the test reside in the product oil. The PCBs in the product solids were negligible when calculating the mass balance. Experience has shown that the PCBs in the product water and recovered triethylamine are also negligible when calculating a PCB mass balance. The mass of PCBs recovered in the oil was calculated by multiplying the weight of oil recovered by the PCB concentration as determined by analysis. The PCB mass balance was as follows:

PCB Balance

<u>Calculated PCBs Input</u>	<u>Calculated PCBs Recovered</u>	<u>Total PCB % Recovery</u>
150 mg	162 mg	108 %

SUMMARY OF MASS BALANCE CALCULATIONS

The following table summarizes the mass balance calculations for each of the constituents considered. The mass balances were based on the amount of the fraction recovered from the simulation divided by the calculated input amount to the simulation.

Mass Balance Summary, %

<u>Solids</u>	<u>Oil</u>	<u>Water</u>	<u>PCBs</u>
101	63	69	108

IV. ECONOMICS

The cost estimate presented in this section is based on the bench-scale treatability test results contained in this report and information provided by Blasland & Bouck Engineers.

Estimate Assumptions:

Amount to be Treated.....10,000 yd³ to 100,000 yd³

Power available at 480V AC (400 amps).

Potable water available for makeup.

Equipment Proposed:

RCC proposes to treat the sediment with a 200-300 tons per day B.E.S.T. Model 615 Unit operated on a 24-hour-per-day basis.

Estimated Costs:

- Mobilization Cost = \$300,000
- @ 10,000 yd³ Treatment Cost = \$155-\$190/yd³
- @ 100,000 yd³ Treatment Cost = \$140-\$170/yd³
- Treatment costs at B.E.S.T. battery limits do not include costs for site excavation, civil work, applicable taxes, pre-screening of feed, overall site management and disposition of the product oil.
- Mobilization costs assume a smooth and level site suitable for unit setup (no foundations required) and direct access to utilities. Mobilization/demobilization costs include all costs to and from the site and all non-processing costs.

V. CONCLUSIONS

The PCB-containing sediment sample from the Sheboygan River is suitable for treatment with the B.E.S.T. solvent extraction process. No problems were observed during testing of the sample.

1. The sample was chemically compatible with triethylamine.
2. The total PCB concentrations in the sample was 170 mg/kg.
3. After treatment, the PCB residual concentration was 0.73 mg/kg, which yields a PCB removal efficiency of 99.6%.
4. The treated solids readily passed the TCLP Toxicity Test for leaching of metals.
5. Virtually all of the PCBs from the sample have been concentrated into the product oil. For each sample, the weight of PCB-containing material was reduced 300 times.

* * * * *